Supporting Information (SI)

Effects of hemicelluloses on dehydrogenative polymerization of monolignols with cationic cell wall-bound peroxidase

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FT-IR Measurement & DS Determination

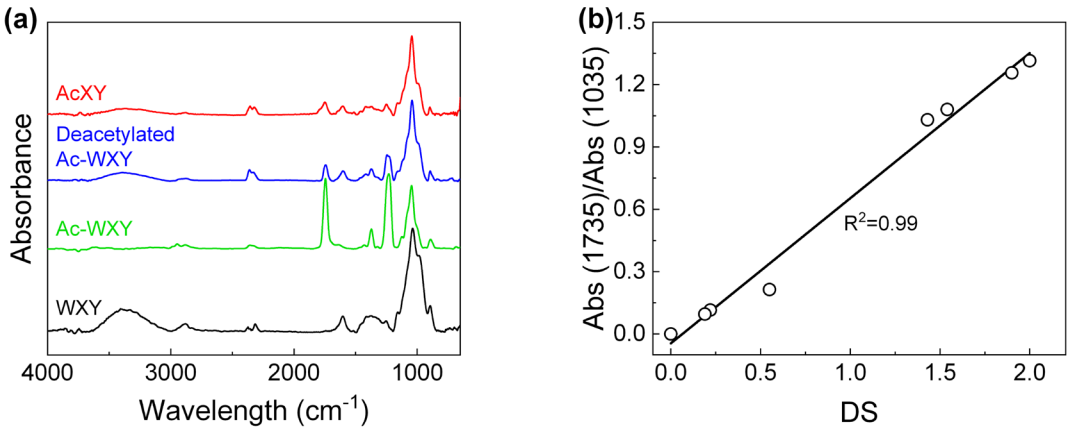

Fig. S1. ATR-mode FT-IR spectra of WXY, fully acetylated WXY (Ac-WXY), partially deacetylated Ac-WXY, and the water-soluble fraction (AcXY) (a) and a standard curve used for DS determination of AcXY (b).

ATR-mode FT-IR measurements. Fourier transform infrared (FT-IR) spectra of WXY and the acetyl derivatives were recorded on an FT/IR-4100 spectrophotometer (Jasco Products Company, Tokyo, Japan), equipped with an attenuated total reflection (ATR) accessory (ATR PRO450-S, Jasco Products Company, Tokyo, Japan). The ATR-mode FT-IR spectra were recorded at room temperature in the wavenumber range of 650–4000 cm^{-1} at a resolution of 4 cm^{-1}.

Determination of DSs. Fully acetylated xylans were partially deacetylated changing the amount of sodium methoxide from 0.30 to 3.6 g to yield partially acetylated xylans with various DSs in the range from 0 to 2. The DSs were determined by following titration method:

The degree of substitution (DS) of Ac-WXY and partially deacetylated xylans was determined by a titration method (1). Each sample (100 mg) was dissolved in 30 mL of acetone/dimethylsulfoxide mixed solvent (4/1, *v/v*) and stirred at room temperature (25 °C) for 16 h. Then, 1 M NaOH solution (5 mL) was added to the solution. After 12 h, the mixture was titrated with 0.25 M H_2SO_4 solution using 1% phenolphthalein as an indicator. The DS was calculated according to the following equation:

$$W/(132 + 42 \times DS) \times DS = 2 \times 0.25 \times (V_0 - V)$$

where W (mg) is the sample weight, and V_0 (mL) and V (mL) are the titration volumes of the blank and sample, respectively. The DS was corrected based on the content of glucuronic acid residues in WXY.

DS calibration curve (Fig. S1b) was made based on the titration results and the absorbance ratio of the carbonyl band at 1735 cm^{-1} to ether band of polysaccharide backbone at 1035 cm^{-1} (2). The DS of AcXY was determined by the FT-IR spectrum (Fig. S1a) using the standard curve, because the sample amount was limited.

SEC Measurement

Molar mass. The number-average molar mass (M_n), weight-average molar mass (M_w), and polydispersity ($Đ_M$) of AcXY and WXY were determined by using a SHIMADZU LC-10 size exclusion chromatography (SEC) system (Kyoto, Japan) equipped with a refractive index (RI) detector. The column was Asahipak GR-7 M HQ series (7.5 mm ID × 300 mm L ×2, Shodex). The eluent was 0.2 M $NaNO_3$ aqueous solution, and the flow rate was 0.5 mL min^{-1}. The column temperature was set at 35 °C. The Mn and Mw were determined by using a calibration curve, which was prepared from authentic pullulan standards.

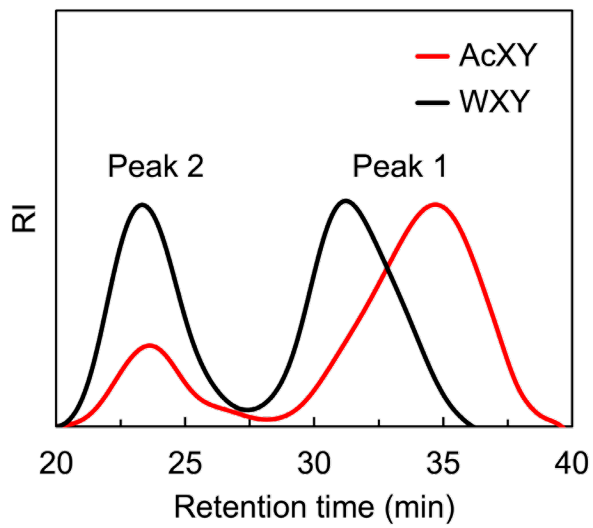

Fig. S2. Size exclusion chromatograms of AcXY and WXY detected by a refractive index detector.

Table S1. Molar mass distributions of AcXY and WXY.

	M_w / kDa		M_n / kDa		$Đ_M$ [a]	
Sample	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
AcXY	16	1080	7.4	718	2.2	1.5
WXY	42	1250	22	820	1.9	1.5

[a] Polydispersity: M_w / M_n.

^{13}C-NMR Measurement

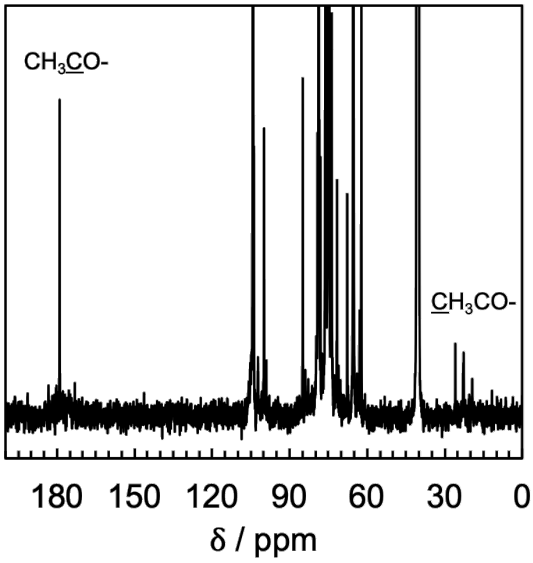

Fig. S3. ^{13}C-NMR spectrum for AcXY measured in deuterium oxide at 50 ºC.

∗The chemical shift at around 40 ppm in Figure S3 is due to the contaminated DMSO.

QCM-D Profiles on HRP Adsorption

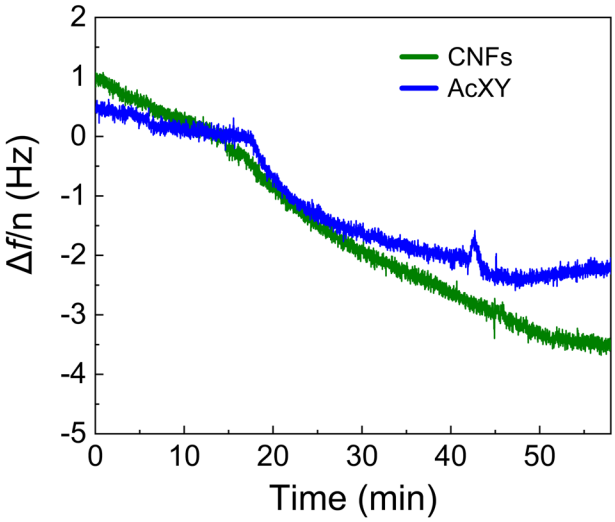

Fig. S4. Δ*f*/n profiles of HRP adsorption on CNFs- and AcXY-coated surfaces.

AFM Observation of the Sensor Surfaces

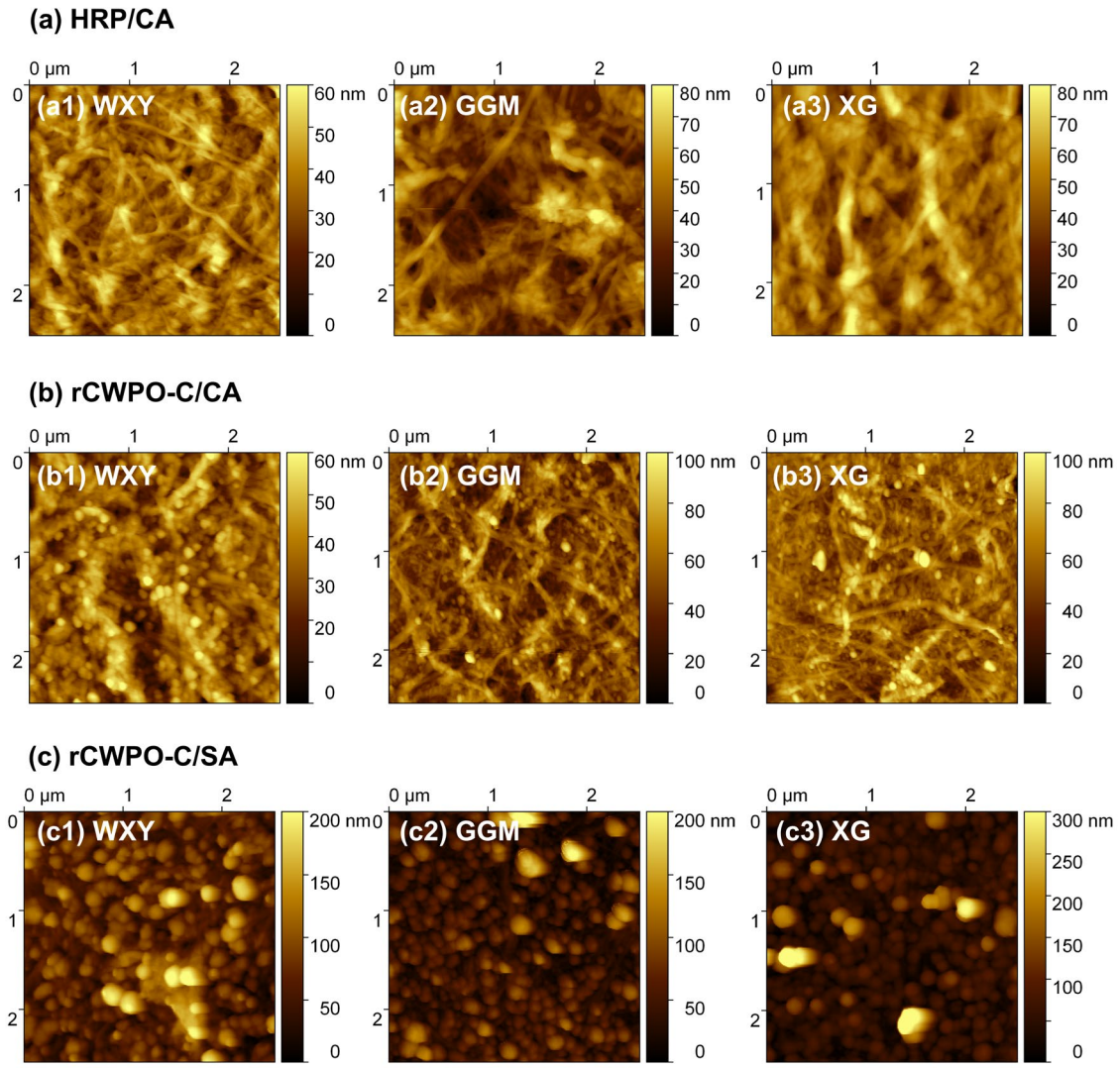

Fig. S5. AFM images of the sensor surfaces coated with WXY, GGM and XG after flowing CA/H_2O_2 on (a) HRP- and (b) rCWPO-C-absorbed sensors, and after flowing (c) SA/H_2O_2 on rCWPO-C-absorbed sensors.

SI References

1. S. Taira, et al., Cellulose acetate with CTA I polymorph can be defibrated into nanofibers to produce a highly transparent nanopaper. Cellulose 27, 4991-5001 (2020).

2. G. Frisoni, et al., Natural cellulose fibers: heterogeneous acetylation kinetics and biodegradation behavior. Biomacromolecules 2, 476-482 (2001).