Supporting Information

Co-design of Combinatorial Organosolv Pretreatment (COP) and Lignin Nanoparticles (LNPs) in Biorefineries

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Table S1 Compositions in pretreated solid from combinatorial organosolv pretreatment (COP) with controlled pH

	Glucan	SD	Xylan	SD	Arabinan	SD	Lignin (AIL)	SD	Lignin (ASL)	SD	Ash	SD	Total
Step 1													
Case 1-5	34.1	0.1	16.0	0.1	1.0	0.2	17.6	0.6	1.7	0.0	8.0	0.0	78.3
Case 6	37.9	1.3	19.0	0.8	0.4	0.0	13.3	2.7	1.2	0.0	1.8	0.0	73.6
Step 2													
Case 1	57.5	0.5	11.0	0.2	0.0	0.0	10.4	1.4	1.1	0.0	8.4	0.0	88.4
Case 2	40.5	1.3	16.4	0.6	0.9	0.2	15.0	0.1	1.5	0.0	6.4	0.0	80.7
Case 3	36.5	0.8	17.8	1.4	1.1	0.1	18.5	0.0	1.6	0.0	7.6	0.0	83.1
Case 4	48.2	0.2	21.6	0.3	1.2	0.0	9.3	0.6	1.2	0.0	8.1	0.0	89.6
Case 5	51.2	1.5	11.1	0.2	0.0	0.0	14.0	0.6	1.1	0.0	6.8	0.0	84.3
Case 6	55.7	0.8	13.4	0.2	0.0	0.0	13.1	0.5	0.8	0.0	2.0	0.0	85.0

AIL represents acid insoluble lignin; ASL represents acid soluble lignin. SD represents standard deviation.
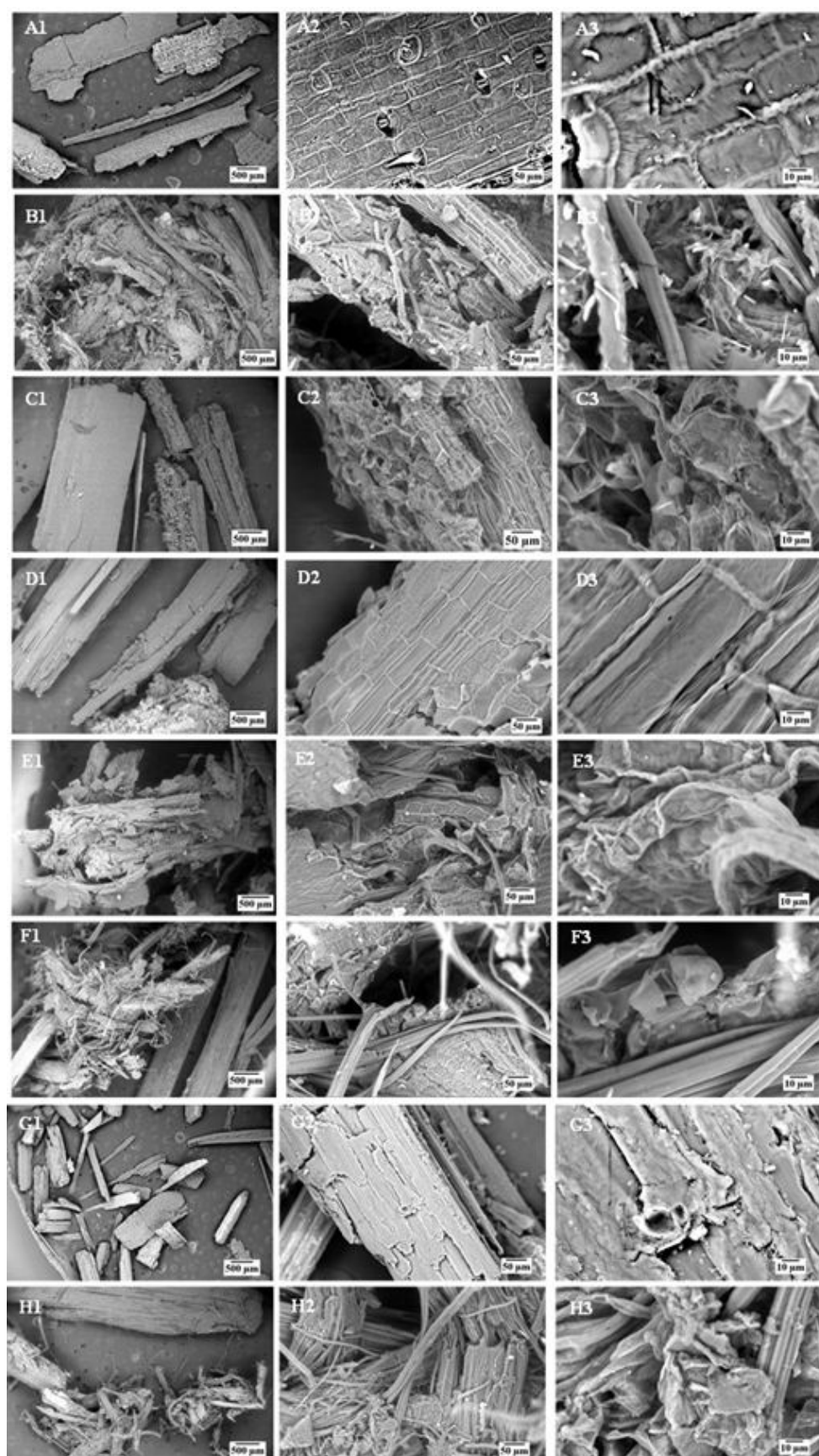
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Figure S1 Scanning electron microscopy (SEM) images of untreated and pretreated corn stover and switchgrass. A1-3, untreated corn stover; B1-3, corn stover pretreated with LHW followed by EtOH+SA; C1-3, corn stover pretreated with LHW followed by EtOH+FA; D1-3, corn stover pretreated with LHW followed by EtOH; E1-3, corn stover pretreated with LHW followed by EtOH+SH; F1-3, corn stover pretreated with LHW followed by MeOH+SA; G1-3, untreated switchgrass; H1-3, switchgrass pretreated with LHW followed by EtOH+SA. Pretreatment strategies were described in Table 1. LHW represents liquid hot water; EtOH+SA represents ethanol plus sulfuric acid; EtOH+FA represents ethanol plus formic acid; EtOH+SH represents ethanol plus sodium hydroxide. Left, middle, and right columns show ~50, 500 and 2000 times magnification, and scale bars of 500, 50 and 10 μm, respectively.
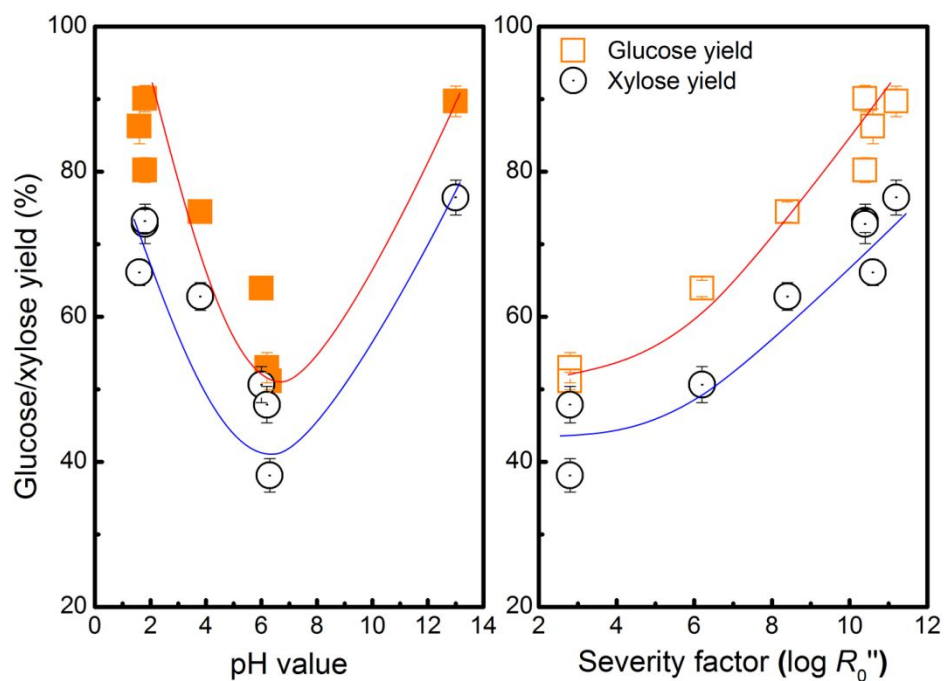
Figure S2 Correlations of glucose/xylose yield with pH value and severity factor of combinatorial organosolv pretreatment (COP) with controlled pH
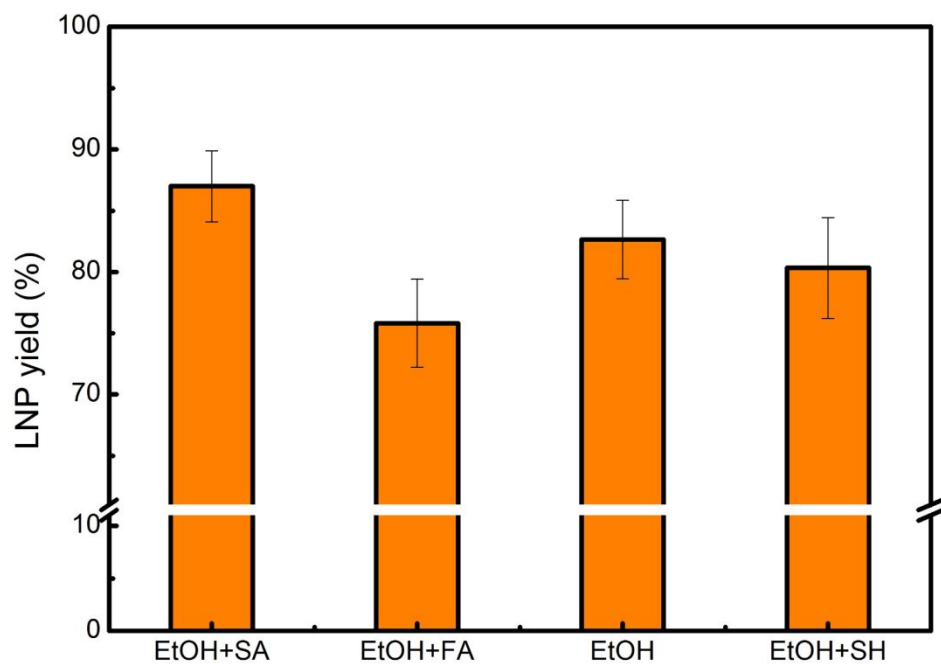
Figure S3 The yield of lignin nanoparticles (LNPs) fabricated from the lignin fractionated by combinatorial organosolv pretreatment (COP) with controlled pH. EtOH+SA represents ethanol plus sulfuric acid; EtOH+FA represents ethanol plus formic acid; EtOH+SH represents ethanol plus sodium hydroxide
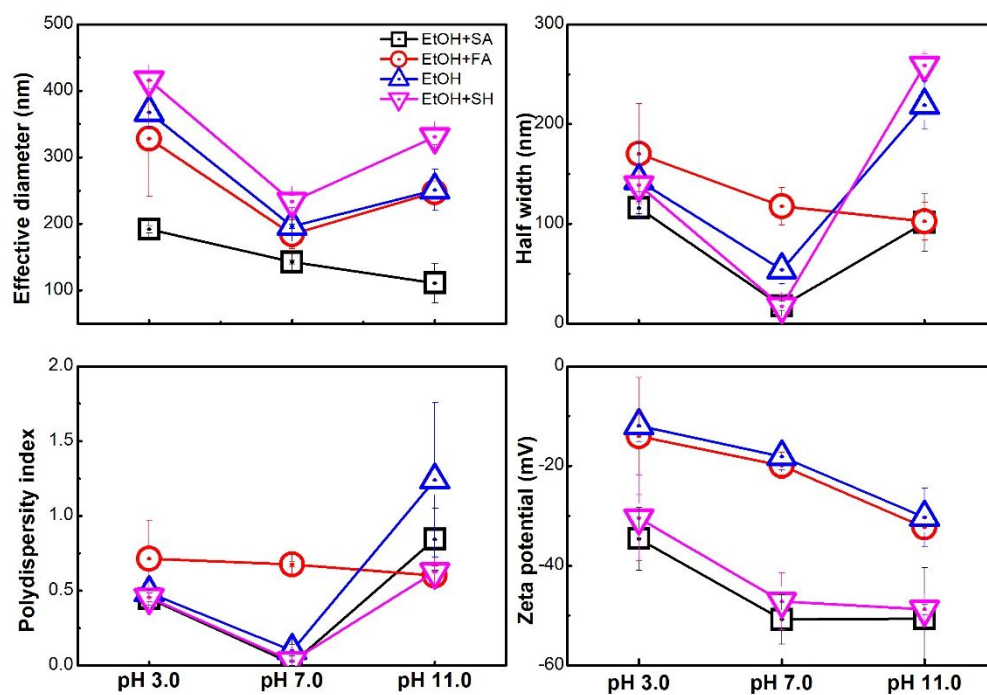
Figure S4 Effects of pH value of the dispersion on the stability of lignin nanoparticles (LNPs) fabricated from the lignin fractionated by combinatorial organosolv pretreatment (COP). Pretreatment strategies were described in Table 1. EtOH+SA represents ethanol plus sulfuric acid; EtOH+FA represents ethanol plus formic acid; EtOH+SH represents ethanol plus sodium hydroxide
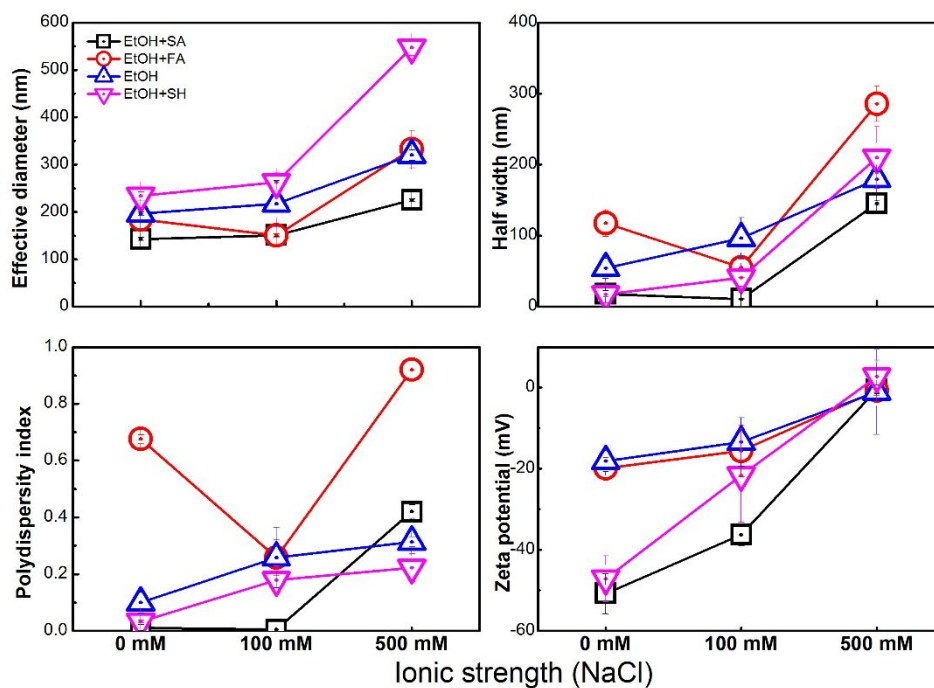
Figure S5 Effects of NaCl concentration on the stability of lignin nanoparticles (LNPs) fabricated from the lignin fractionated by combinatorial organosolv pretreatment (COP). Pretreatment strategies were described in Table 1. EtOH+SA represents ethanol plus sulfuric acid; EtOH+FA represents ethanol plus formic acid; EtOH+SH represents ethanol plus sodium hydroxide
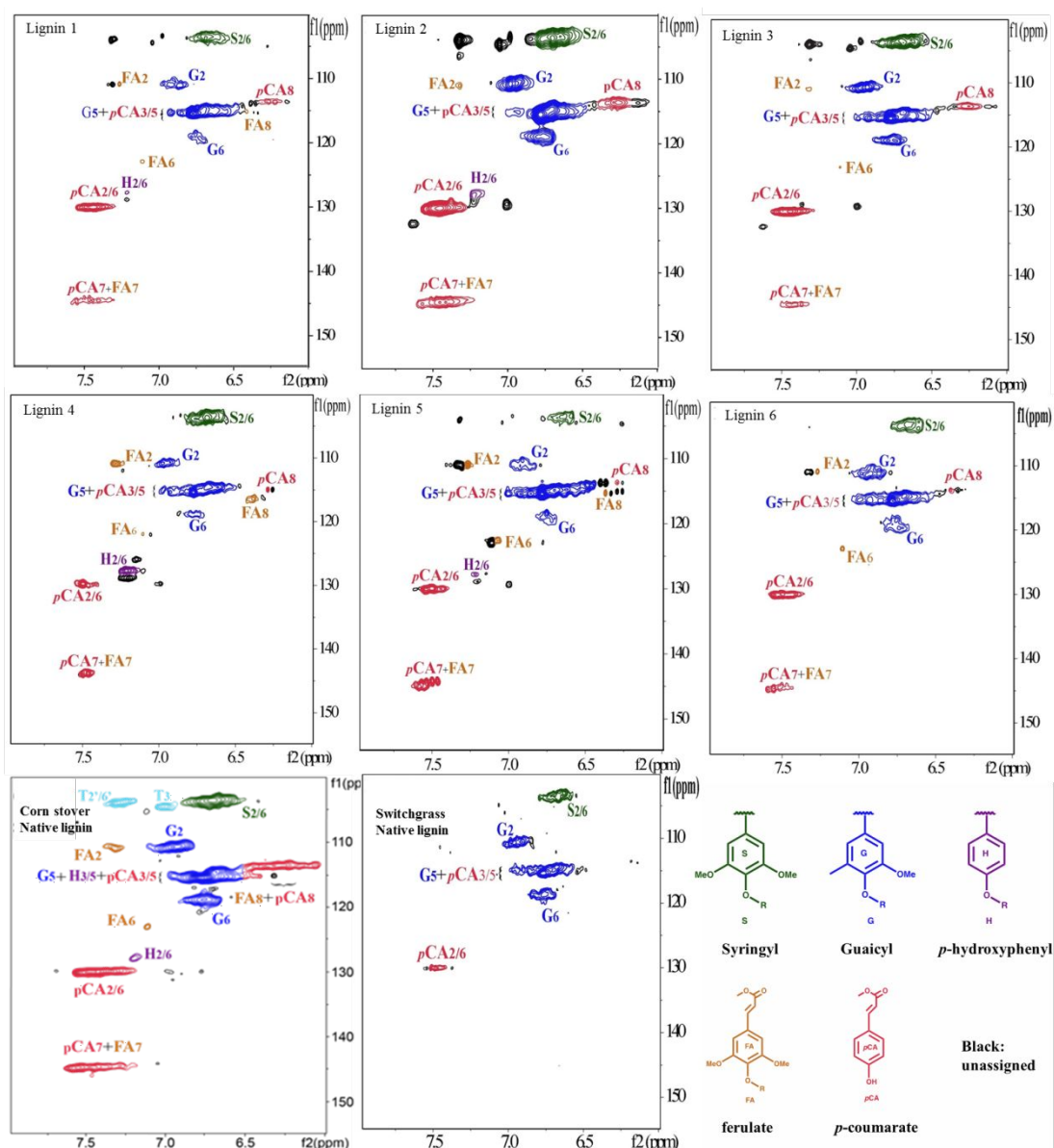
Figure S6 Aromatic and lignin interunit regions of 2D HSQC NMR spectra of the fractionated lignin from each combinatorial organosolv pretreatment (COP). Lignin 1 represents the fractionated lignin produced by COP Case 1 described in Table 1. Lignin 1-5 was fractionated from corn stover while lignin 6 was fractionated from switchgrass
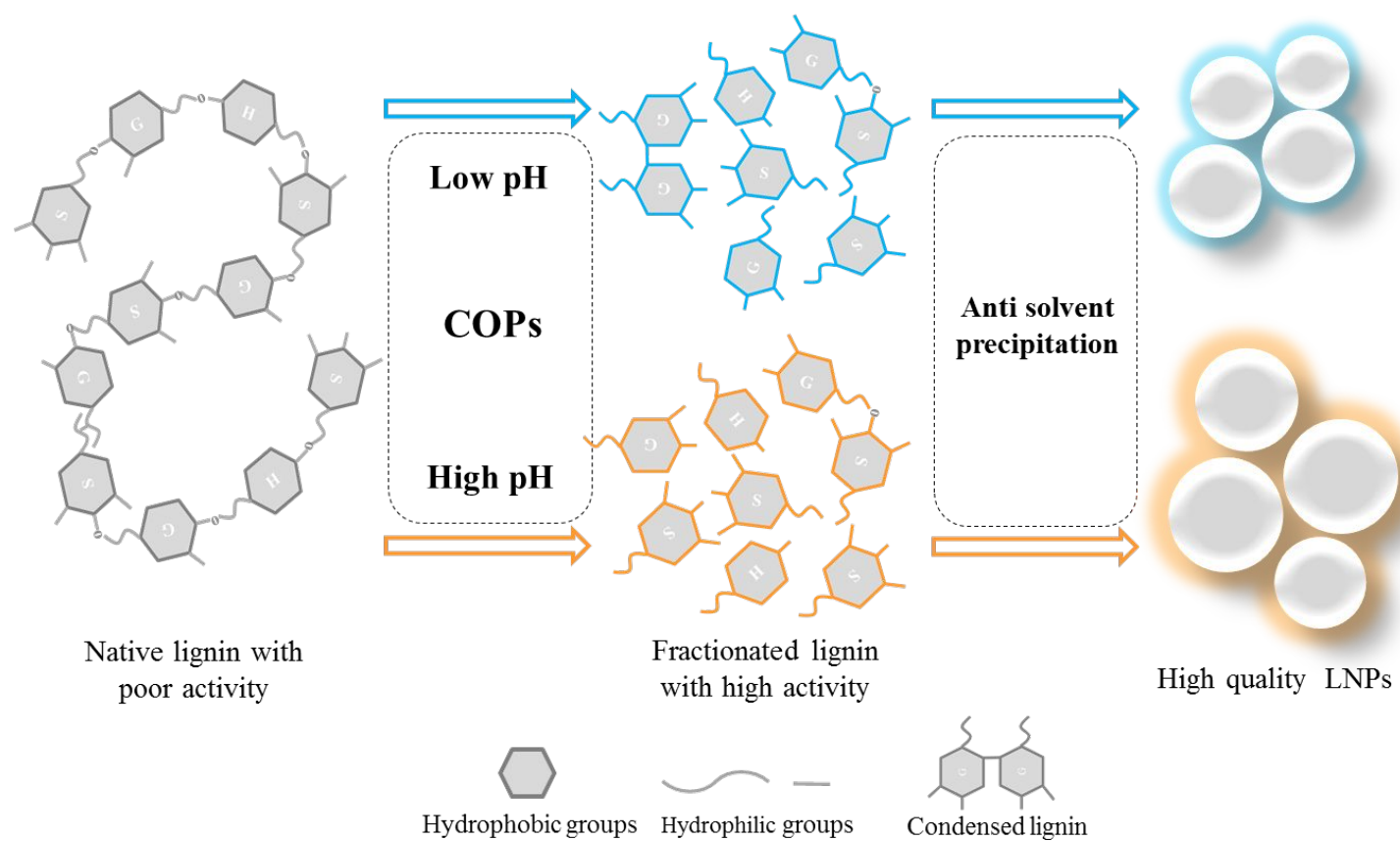
Figure S7 Proposed formation mechanism model of lignin nanoparticles (LNPs) from corn stover lignin produced by combinatorial organosolv pretreatment (COP) with controlled pH.