Electronic Supplementary Material (ESI)

Sustainable production of catechol derivatives from waste Tung nutshells C/G-type lignin by heterogeneous Cu-NC catalytic oxidation

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Materials and reagents

Tung nutshell was peeled from the Tung seed (Rongan Forestry of Guangxi Province) and ground into powder (100 mesh). carbon black XC-72R (CABOT), HNO_3 solution (65%-68 %, Guangzhou chemical reagents), $Co(OAc)_2 \cdot 2H_2O$ (99.5%), $Cu(OAc)_2 \cdot 2H_2O$ (99.0%), $Fe(OAc)_2OH \cdot H_2O$ (AR), $MoO_2(acac)_2$ (97%), $CuSO_4 \cdot 5H_2O$ (99.8%), $CuCl_2 \cdot 2H_2O$ (99.99%, Aladdin), $Mn(OAc)_3 \cdot 2H_2O$(98%, Bidepharm), 2,6-dimethoxyphenol (99%, Alfa Aesar), acetonitrile (99.0%, Guangzhou chemical reagents), protocatechuic acid, protocatechuic aldehyde, vanillic acid, vanillin, furfural, 1,4-dioxane, DMF, DMSO-d_6 (99.9% D + 0.03% TMS), acetonitrile and tetrahydrofuran eluent, were purchased from Macklin Biochemical Technology Co. All commercial reagents, unless otherwise noted, were used without further treatment.

Feedscock preparation

To produce Tung nutshell powder feedstocks (150 mesh), The Tung seeds were dried and peeled to obtain the bulk seed coats. After ultrasonic washing with $EtOH/H_2O$, the dried seed coats were ground into powder and then sieved by the 150 mesh sieve.

Drying   Peeling   Washing   Grinding   Sieving
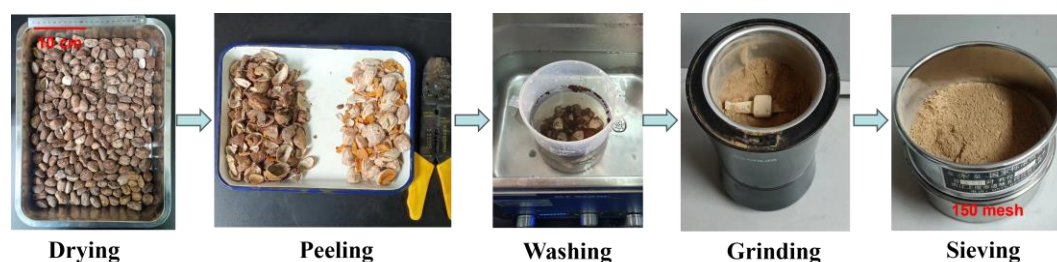
Scheme S1. treating processes of the feedstocks

2D HSQC NMR analysis

The preparation of samples was as follows: To obtain the oxidized lignin oil, the mixture was filtered then concentrated to remove the solvent, and finally vacuum dried at 50 °C for 48 h. The dried oxidized lignin oil (40 mg) or 10 mg of monomers (vanillin et al.) dissolved in 0.5 mL of DMSO-d_6 before the test. The results are obtained based on repeated experiments. The 2D Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance (2D HSQC NMR) spectra were collected on a Buker DRX-600 NMR spectrometer using the standard Bruker pulse sequence hsqcetgpsi.2. The test parameters: The spectral width of f2 (^{1}H) dimensions (10.5 ppm, center at 4.8 ppm), the spectral width of f1 (^{13}C) dimensions (165 ppm, center at 75 ppm), receiver gain of 101, acquisition time of 130 ms, relaxation delay time of 1.5 s, scan times of 24, and data points of 1024. The spectra were processed by MestReNova software using a squared cosine bell in both f1 and f2 dimensions. The peak of DMSO-d_6 (δ_C/δ_H = 39.52/2.49 ppm) was used as the signal correction.

## Organosolv Lignin extraction method

Pretreatment: the Tung nutshell powder should be pretreated before extraction in the organic solvent. Specifically, the powder was washed with the toluene/ethanol co-solvent (2/1, v/v) in a Soxhlet extractor at 105 °C for 12 h to remove the fat, waxes, and other residuals. After cooling to room temperature, the solid was washed with ethanol and dried at 80 °C to obtain the pretreated tung nutshell powder. The extraction procedure is as follows: 3.0 g of pretreated tung nutshell powder and 36 mL of ethanol/H_2O（6:4，v/v）mixture were added to a Teflon insert reactor. After sealing, the reactor was replaced with N_2 then fed with 1 MPa of N_2. Then the temperature in the reactor was raised to 180 °C and maintained for 200 min with stirring. When the reaction was over, the reactor was cooled in the ice-bath. The mixture was filtrated to collect the filtrate. And the filter cake was washed with 36 mL of ethanol/H_2O（6:4，v/v）. 100 mL of H_2O was added to the collected filtrate with stirring for 2 h, during which solid precipitation would occur. The mixture was filtrated to collect the precipitation. Finally, the solid dried at 45 °C for 24 h to give a purified organosolv lignin.

Lignin Content

Based on the two-stage H_2SO_4 hydrolysis process by NREL/TP-510-42618 protocol,[1, 2] The content of Klason lignin in tung nutshell powder was determined. The powder was dried at 105 °C for all night before pretreatment. Then the powder (5.00 g) was washed with the toluene/ethanol co-solvent (2/1, v/v) in a Soxhlet extractor at 105 °C for 12 h to remove the fat, waxes, and other residuals. After cooling to room temperature, the solid was washed with ethanol and dried at 80 °C to obtain the pretreated tung nutshell powder (4.14 g). Under an ice-water bath condition, H_2SO_4 (15 mL, 72%, w/w) was added slowly to the above extracted tung nutshell (1.00 g). After the suspension was stirred in 30 °C water bath for 2 h, deionized water (420 mL) was added, diluted the H_2SO_4 (72%) to 4% for the second hydrolysis. Afterwards, the above solution refluxed at 120 °C for 6 h, and the residual was filtered and washed to neutrality by water. Finally, the solid was dried at 105 °C for all night (0.59 g). The residual weight is denoted as W_h. The lignin content was calculated as follows:

$$Lignin \ (wt \ \%) = \frac{W_h}{W_e} \times 100\%$$

where W_e and W_h are the mass of the extracted tung nutshell powder and the residual solid after H_2SO_4 hydrolysis, respectively. Then Klason lignin content was 59 wt % based on the extracted tung nutshell powder, and 49 wt % based on the raw tung nutshell powder. The results are obtained based on repeated experiments.
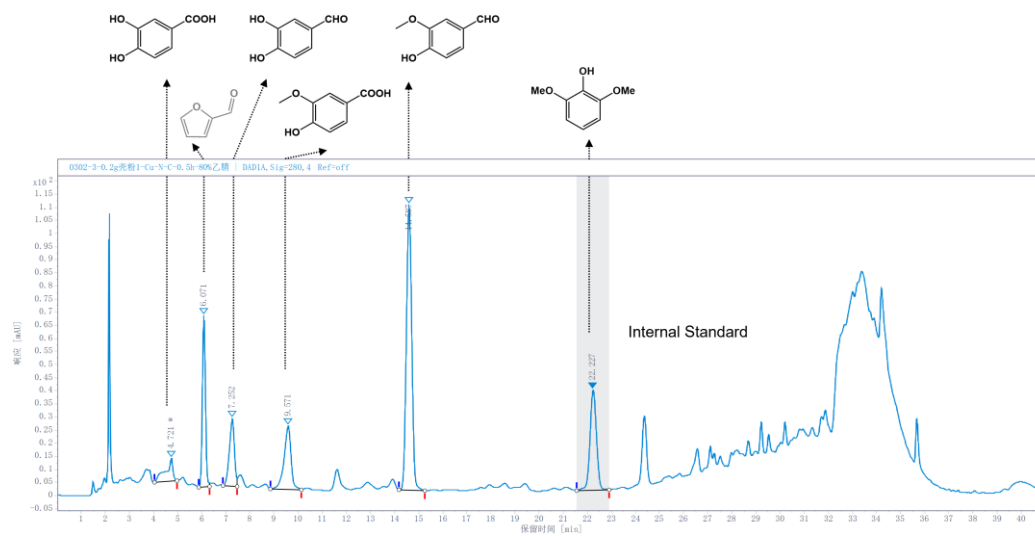
Figure S1. HPLC result of the Cu-NC-800 catalytic oxidative reaction. Conditions: Tung nutshell (0.2 g), Cu-NC-800 catalyst (20 mg), CH$_3$CN/H$_2$O (8/2, v/v, 20 mL), Air (2 MPa), 190 ºC, 1 h.

Table S1. Yields of lignin-derived monomers from blank and the Cu-NC-800 catalyst.

Entry	Catalyst	Aromatic monomer yield (mg/g)				Total	Furfural
		Vanillic acid	Vanillin	Protocatechuic acid	Protocatechuic aldehyde		
1	None	14.6	14.8	/	0.7	30.1	3.3
7	Cu-NC-800	22.2	19.2	1.9	0.2	43.5	2.0

Conditions: Tung nutshell (0.2 g), catalyst (20 mg), CH_3CN/H_2O (8/2, v/v, 20 mL), Air (2 MPa), 190 ^{o}C, 4 h.

Note: The special solvent system and reaction atmosphere may be key factors in generating a high blank yield. In our previous work,[3] the solvent effect is obvious in the oxidative catalytic fractionation of native Tung nutshell. Several common solvents could effectively influence the catalytic activity, and their yields of aromatic monomers were in the following order: H_2O < DMF < GVL < CH_3OH < 1,4-dioxane < CH_3CN. The CH_3CN solvent was found to give the highest yield, and the blank yield is 24.0 mg/g in CH_3CN. Furtherly, a suitable CH_3CN/H_2O ratio could enhance the activity. Water could assist in the release of lignin from native lignocellulose at 190 ^{o}C. On the other hand, once the air atmosphere in the reactor was replaced with an N_2 atmosphere, the total yield decreased to 6.0 mg/g. The significantly reduced activity demonstrates that an O_2 atmosphere is essential. Therefore, the solvent system and reaction atmosphere may be key factors in generating a high blank yield.

For the homogeneous process reported by a previous study,[3] 0.1253 mmol of copper salt was added, with an optimal yield of 60.8 mg/g for 4 h. Therefore, mole specific activity of the copper chloride catalyst was 121.3 $mg*g^{-1}*mmol^{-1}*h^{-1}$. In the current study, the Cu-NC-800N catalyst affords a 43.5 mg/g yield of aromatic monomers under identical conditions. Based on the Cu content (4.2 wt %, ICP analysis), the mole-specific activity of the Cu-NC-800N catalyst was 823.9 $mg*g^{-1}*mmol^{-1}*h^{-1}$, indicative of a significant advantage. On the other hand, for the homogeneous process, both the aromatic products and copper salt were dissolved in the CH_3CN/H_2O co-solvent, which made it hard to achieve their separation. However, liquid aromatic products could be effectively separated from the solid mixture by a simple filtration for the heterogeneous catalytic system. With this regard, the heterogeneous catalytic system has much improvement compared with the homogeneous systems.
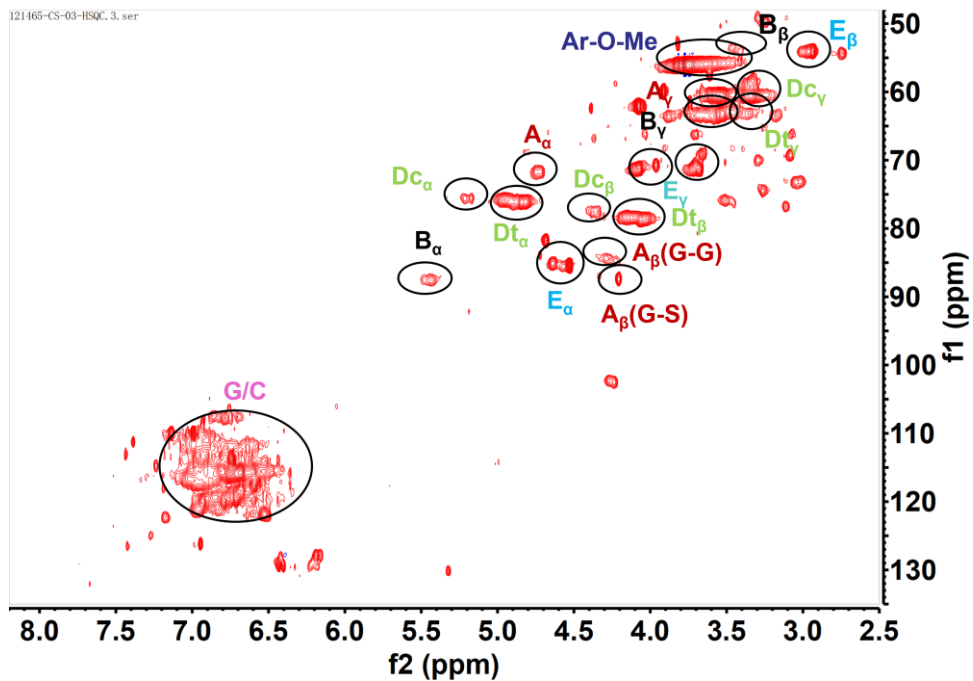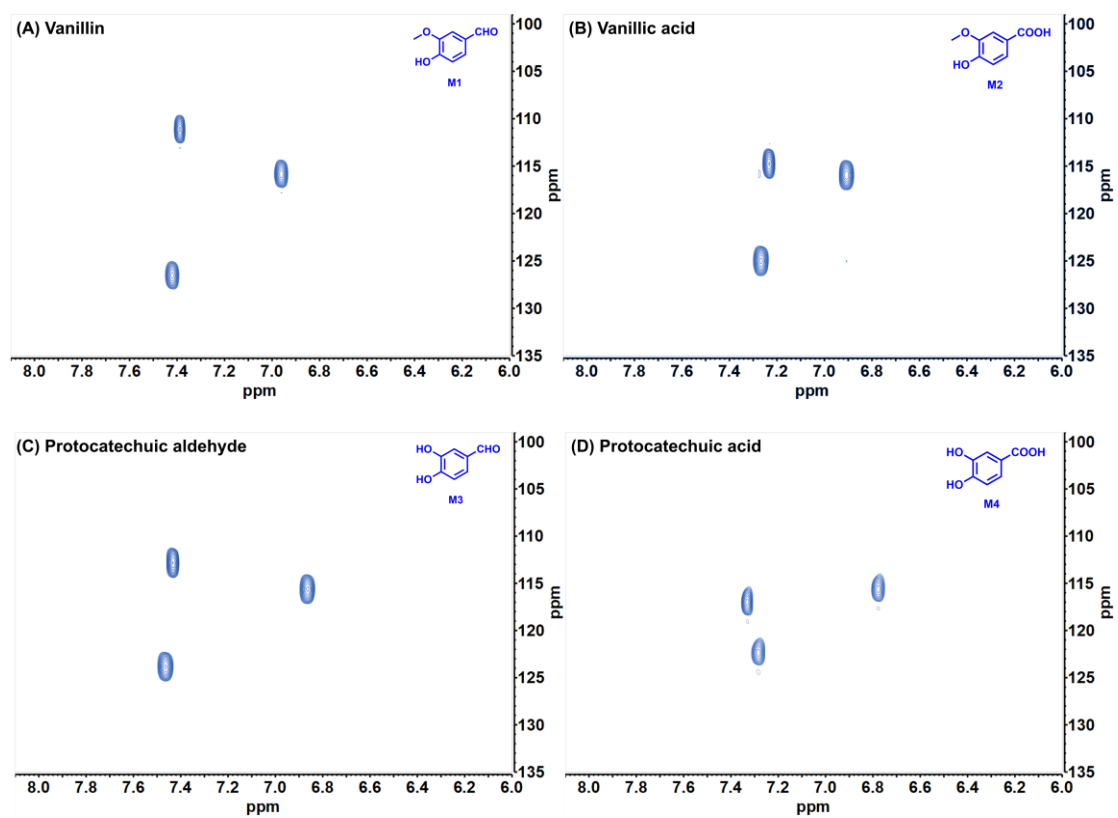
Figure S2. The 2D HSQC NMR spectra of Tung nutshell lignin oils for the blank experiment under N_2. Conditions: Tung nutshell (0.2 g), CH_3CN/H_2O (8/2, v/v, 20 mL), N_2 (2 MPa), 190 °C, 4 h.
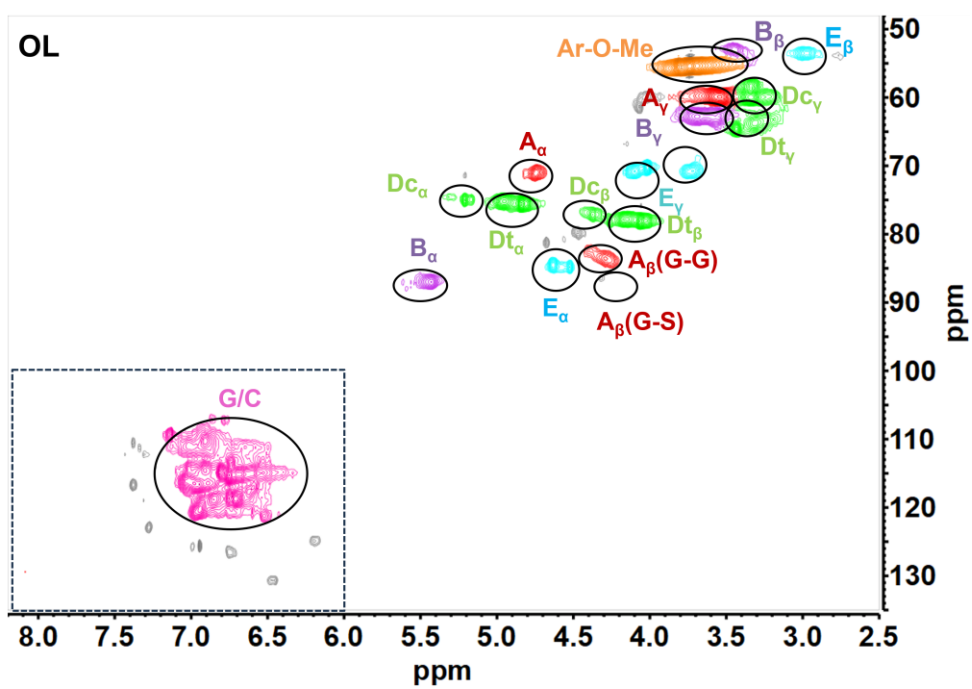
Figure S3. The 2D HSQC NMR spectra of Tung nutshell organosolv lignin (OL)

Figure S4. The 2D HSQC NMR spectra of (A)-(D) vanillin, vanillic acid, protocatechuic aldehyde, and protocatechuic acid standard substance, respectively.

Table S2. 2D HSQC NMR data for the signal assignments.[4-7]

Feature regions	δ_C/δ_H (ppm)	Characteristic Groups	δ_C/δ_H (ppm)	Characteristic Groups
Alkyl linkage structure on the side chain of aromatics (δ_C/δ_H = 50-100/2.5-6.0 ppm)	56.37/3.74	Ar-OCH$_3$	72.35/4.89	C$_\alpha$-H$_\alpha$ of β-O-4 (A)
	84.25/4.31, 86.66/4.13	C$_\beta$-H$_\beta$ of β-O-4 (A)	60.22/3.71	C$_\gamma$-H$_\gamma$ of β-O-4 (A)
	87.66/5.42	C$_\alpha$-H$_\alpha$ of β-O-4 (B)	53.74/3.46	C$_\beta$-H$_\beta$ of β-O-4 (B)
	63.35/3.71	C$_\gamma$-H$_\gamma$ of β-O-4 (B)	85.69/4.65	C$_\alpha$-H$_\alpha$ of β-O-4 (E)
	54. 11/3.07	C$_\beta$-H$_\beta$ of β-O-4 (E)	71.75/3.82, 71.75/4.18	C$_\gamma$-H$_\gamma$ of β-O-4 (E)
	75.67/5.24	C$_\alpha$-H$_\alpha$ of *cis*-benzodioxane (D$_c$)	77.76/4.40	C$_\beta$-H$_\beta$ of *cis*-benzodioxane (D$_c$)
	60.64/3.38	C$_\gamma$-H$_\gamma$ of *cis*-benzodioxane (D$_c$)	76.21/4.86	C$_\alpha$-H$_\alpha$ of *trans*-benzodioxane (D$_t$)
	78.76/4.09	C$_\beta$-H$_\beta$ of *trans*-benzodioxane (D$_t$)	65.30/3.44	C$_\gamma$-H$_\gamma$ of *ttrans*-benzodioxane (D$_t$)
aromatics units (δ_C/δ_H = 100-135/6.0-8.0 ppm)	110.99/6.92, 115.21/6.76, 119.48/6.59	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of G unit	117.33/6.97, 116.02/6.77, 120.79/6.95	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of C unit
C/G monomers (δ_C/δ_H = 100-135/6.0-8.0 ppm)	115.74/6.96, 118.08/7.39, 126.55/7.42	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of vanillin	114.71/7.23, 115.91/6.91, 124.98/7.27	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of vanillic acid
	112.83/7.43, 115.60/6.86, 7.47/123.88	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of protocatechuic aldehyde	117.06/7.33, 115.55/6.77, 122.30/7.28	C$_2$-H$_2$, C$_5$-H$_5$ or C$_6$-H$_6$ of protocatechuic acid
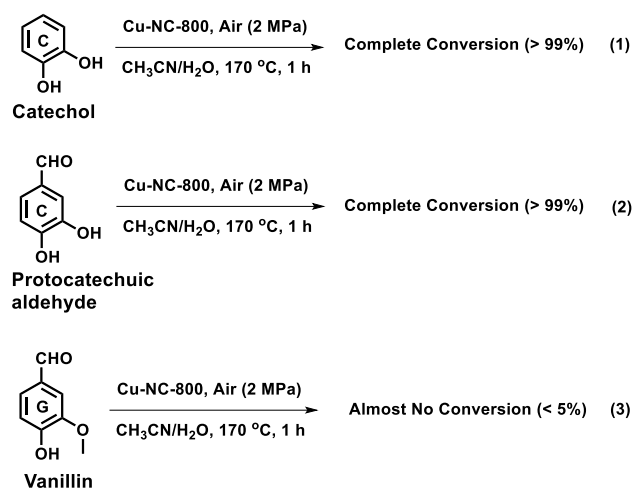
Scheme S2. control experiments with representative model compounds.

Note: In the Cu-NC-800 catalytic oxidative system, both the catechol-type aromatics (catechol or protocatechuic aldehyde) were completely transformed and we did not detect effective products. The very low carbon balance of C-type aromatics oxidation process might be due to degradation or transformation of the aromatic ring, with the formation of undetected active intermediates or low molecular weight carboxylic acids.[8-10] For comparison, almost no reaction occurred for the vanillin model substrate under identical conditions, which might mean a Fenton-like reaction did not occur for the G-type monomers. Above significant differences between the C-type and G-type monomers could account for the product distribution of the four catechol derivative aldehydes, and acids. Besides the degradation or transformation of the catechol-type aromatics by the Fenton-like oxidation could contribute to the reduced signal intensity for the aromatic regions of 2D HSQC NMR results.
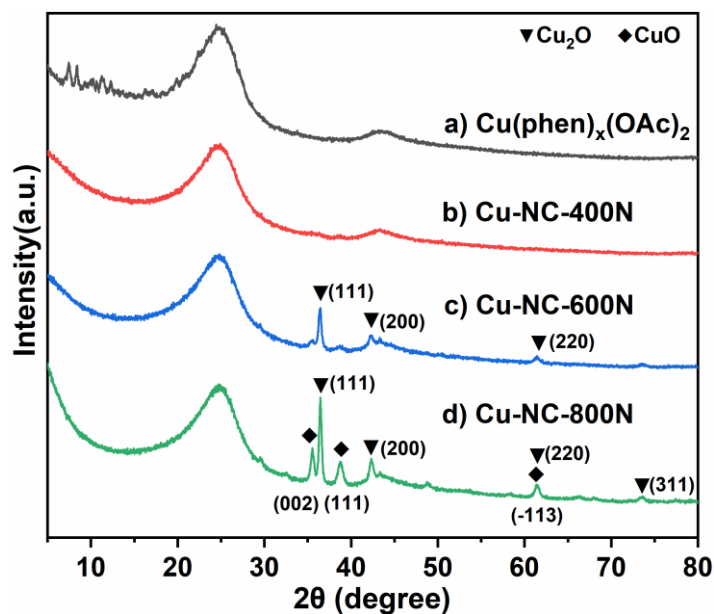
Figure S5. XRD of the different samples.

Note: As shown in XRD patterns, no obvious diffraction peaks appeared for the $Cu(Phen)_x(OAc)_2$ sample, possibly indicative of an amorphous structure. The Cu-NC-400N sample shows a similar XRD pattern, indicating precursor calcination at such a low temperature (400 ^oC) did not decompose or only a small amount of decomposition occurred. When calcination at a higher temperature of 600 ^oC, a set of weak signals of Cu_2O appeared for the Cu-NC-600N sample, indicating metal precursor partially decomposed to form the Cu_2O species. For the Cu-NC-800N sample, two sets of characteristic diffraction peaks could be easily recognized. 2θ of 36.4°, 42.3° and 61.3° (marked with a triangle) were assigned to the (111), (200), (220) lattice plane of Cu_2O, while 35.5° and 38.7° (marked with a square) were ascribed to the (002), (111) lattice plane of CuO, which indicated that Cu(II) of CuO and Cu(I) of Cu_2O was coexisting in the Cu-NC-800N catalyst.
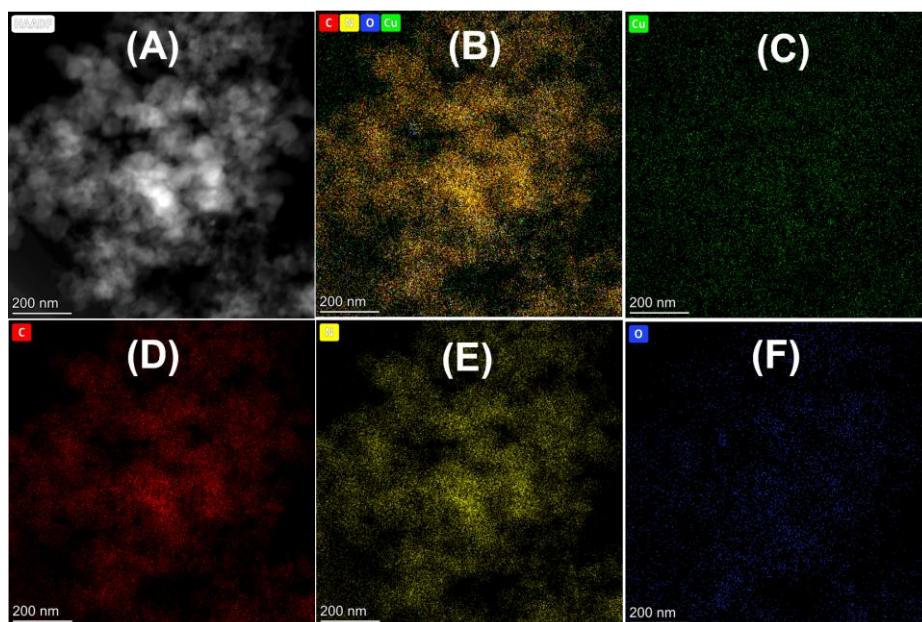
Figure S6. STEM-HAADF image of (A) Cu-NC-400H, and corresponding HRTEM-EDX mapping images of (B)-(F) Cu, C, N, and O of Cu-NC-400H sample.
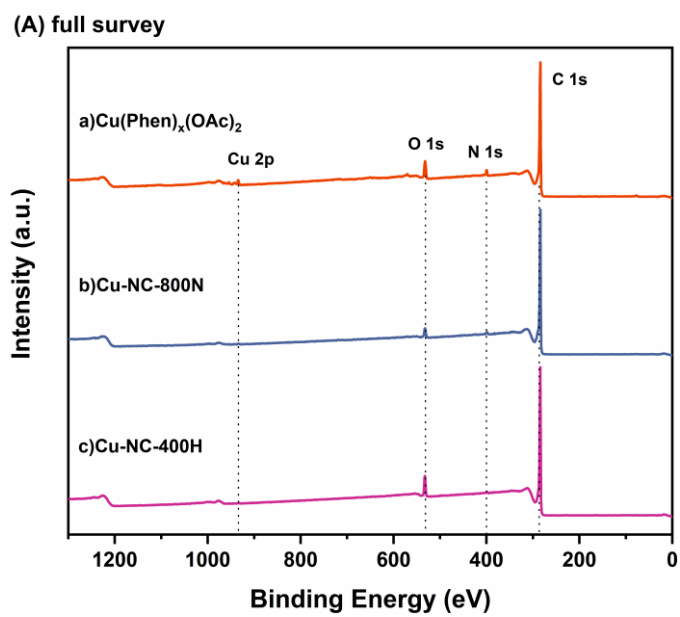
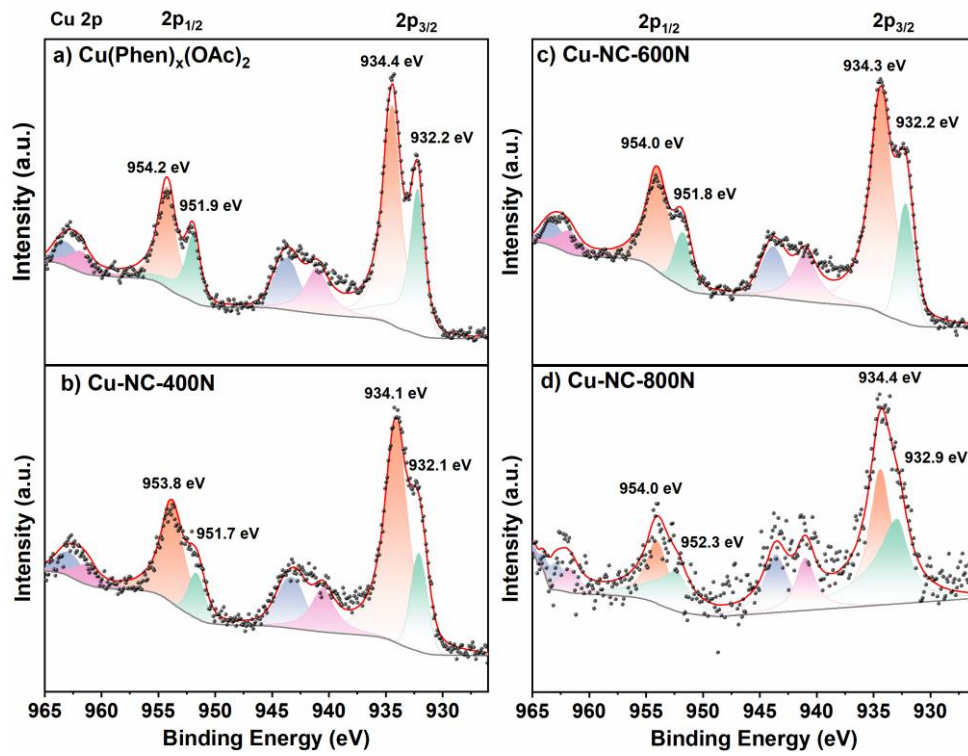**Figure S7.** The XPS full survey of a) $Cu(Phen)_x(OAc)_2$, b) Cu-NC-800N, and c) Cu-NC-400H sample.

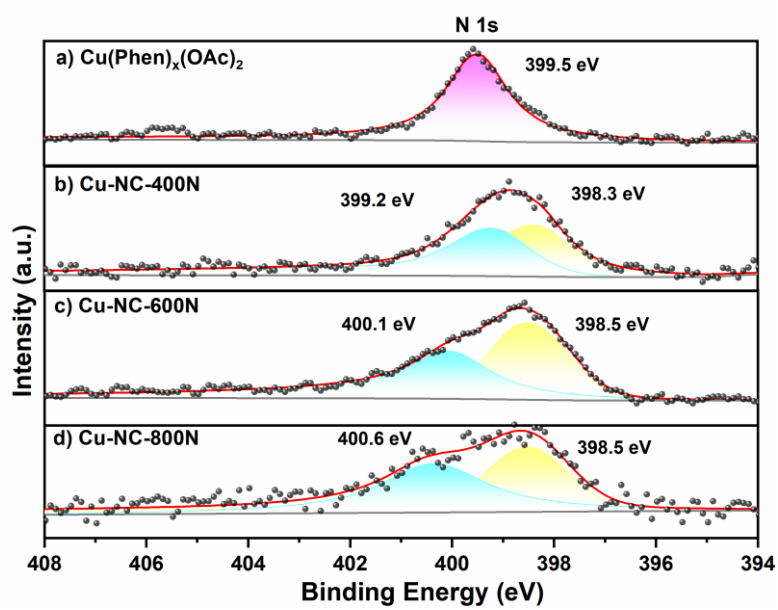**Figure S8.** Cu 2p XPS signal of different samples.

Figure S9. N 1s XPS signal of different samples

References

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