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Supplementary Materials for

Electrochemical Conversion of Lignin to Short-Chain Carboxylic Acids

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Figs. S1 to S9



Fig. S1. Three types of aromatic structures in lignin followed by radical coupling to produce a lignin fragment. In plant cell walls, lignin is biosynthesized by radical coupling between three primary precursors, *i.e.*, *p*-coumaryl (4-hydroxycinnamyl), coniferyl (4-hydroxy-3methoxycinnamyl), and sinapyl (4-hydroxy-3,5-dimethoxycinnamyl) alcohols. The structural units of lignin were named *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) after the biosynthesis. The intramolecular linkages of lignin mainly include C-O bonds (β -O-4, α -O-4, α -O- γ , 4-O-5) and C-C (β -5, β - β , β -1, 5-5) bonds. Among these bonds, β -O-4 linkage accounts for the highest content in natural lignin ^{1,2}.



Fig. S2. Oxygen-doping carbon black (O-CB) for 2e⁻-ORR. (A) X-ray photoelectron spectroscopy (XPS) survey scans of oxygen-doping carbon black (O-CB) catalysts with different oxygen contents. The oxygen content of 2.09 % was commercial carbon black (XC-72R, Cabot, USA). (B) Faradaic efficiencies of O-CB catalysts with different oxygen contents measured with O-CB//H₂SO₄//Pt/C cell.



Fig. S3. XPS characterization of O-CB (6.83 %) catalyst. The C *1s* spectrum (A) could be deconvoluted into sp^2 carbon at 284.79 eV with a content of 52.63 %, sp^2 carbon/C-O-C/C-O-H at 285.66 eV with a content of 30.52 %, HO-C=O at 288.94 eV and π - π transition at 291.63 eV with the contents of 10.01 % and 6.84 %, respectively. The O *1s* spectrum (B) could be deconvoluted into three contributions, including C=O (831.96 eV), C-O-C/C-O-H (533.62 eV), and adsorbed water (537.09 eV) with the contents of 41.71 %, 53.48 %, and 6.84 %, respectively ^{3, 4}. The High-resolution XPS spectra of Carbon *1s* (A) and Oxygen 1*s* (B) indicate that simple nitric acid treatment could dope oxygen on the surface of carbon black.



Fig. S4. The performance of 2e⁻-ORR activity of O-CB (6.83 %). (A) Linear sweep voltammetry (LSV) of the O-CB (6.83 %) catalysts (bottom panel) measured at 1600 rpm and a scan rate of 0.005 V s⁻¹, coupling with the determination of H_2O_2 on the ring electrode (upper panel) at a fixed potential of 1.2 V vs. RHE. (B) The calculated H_2O_2 selectivity of the O-CB (6.83 %) catalysts determined by the RRDE in 0.1 M Na₂SO₄ electrolyte.



Fig. S5. Morphology characterization of TS-1 zeolites: (A-C) SEM images, and (D-F) elemental mapping images. Based on the results of the EDS analysis, the weight contents of Si and Ti elements were determined to be 96.12 % and 3.88 %, respectively.



Fig. S6. Powder XRD pattern of TS-1 zeolites. The figure shows the intense peaks at $2\theta^{\circ}$ = 7.51, 8.40, 14.31, 20.41, 21.79, 22.60, 23.42, 23.95, 25.37, 26.43, 29.44, 37.06 and 45.00 with corresponding planes (101), (200), (112), (331), (023), (150), (511), (250), (323), (004), (621), (561), (852). The planes (150) and (511) indicate the presence of ordered orthorhombic MFI topology TS-1 framework ⁵.



Fig. S7. Synthesis route of β -O-4 lignin model compound of 2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol (SG). The as-synthesized model compound was obtained as a mixture containing the *erythro* and *threo* isomers. Reagents and conditions were as follows: (1) Br₂, C₂H₅OH, rt, (2) K₂CO₃, acetone, 40°C, (3) HCHO, THF, K₂CO₃, 35°C, (4) NaBH₄, C₂H₅OH, rt.



Fig. S8. Experimental scheme for determining the configurations of β -O-4 models (E or T) by ozonation method. The *erythro/threo* ratio of the obtained β -O-4 model compound was determined by ozonation analysis according to the method developed by Akiyama et al. ^{6, 7}. The trimethylsilyl derivatives were injected into gas chromatography (Shimadzu 17A, GC-FID) with an InertCap 1 column (GL Science NB1, 0.25 mm i.d. × 30 m) to determine the yields of erythronic acid and threonic acid. The two peaks of trimethylsilylated erythronic and threonic acid in the ozonation products found in the GC chromatography were quantified to determine the *erythro/threo* ratio of the obtained mixture of the β -O-4 model compound. The *erythro/threo* ratio was quantified as 7:3.



Fig. S9. Oxidation of monomeric lignin model compounds with and without phenolic hydroxyl groups (compound 1 and 2), and dimeric lignin model compounds (compound 3 and 4). Compound 3 was a non-phenolic model used as a mixture of the *erythro* and *threo* isomers with a ratio of 7:3 bearing both syringyl and guaiacyl nuclei. Compound 4 was a phenolic model with a hydroxyl group at the syringyl nucleus.

References:

- 1. S. Shimizu, T. Yokoyama, T. Akiyama and Y. Matsumoto, J. Agric. Food. Chem., 2012, 60, 6471-6476.
- 2. C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, Chem. Rev., 2015, 115, 11559-11624.
- 3. A. J. Plomp, D. S. Su, K. P. d. Jong and J. H. Bitter, J. Phys. Chem. C, 2009, 113, 9865-9869.
- K. A. Wepasnick, B. A. Smith, J. L. Bitter and D. Howard Fairbrother, *Anal. Bioanal. Chem.*, 2010, 396, 1003-1014.
- B. Wang, X. Peng, W. Zhang, M. Lin, B. Zhu, W. Liao, X. Guo and X. Shu, *Catal. Commun.*, 2017, 101, 26-30.
- 6. T. Akiyama, T. Sugimoto, Y. Matsumoto and G. Meshitsuka, J. Wood Sci., 2002, 48, 210-215.
- T. Akiyama, H. Goto, D. S. Nawawi, W. Syafii, Y. Matsumoto and G. Meshitsuka, *Holzforschung*, 2005, 59, 276-281.