

Supporting Information

One-pot oxidation-acetalization strategy for photocatalytic cleavage of C-C bonds in lignin model compounds over phosphorus-doped carbon nitride

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Supplementary Tables

Table S1. The physicochemical properties of different catalysts.

Sample	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{p}^{b} ($\text{cm}^3 \cdot \text{g}^{-1}$)	PD ^c (nm)	C content ^d (at.%)	N content ^d (at.%)	P content ^d (at.%)	P content ^e (wt.%)
GCN	6.07	0.05	27.6	44.3	55.7	/	/
P _{1,2} -CN	19.54	0.12	25.7	43.7	54.8	1.5	11.6

^aBET surface area. ^bPore volume. ^cAverage pore diameter. ^dDetermined by XPS analysis.

^eDetermined by ICP-OES.

Table S2. Elemental composition and chemical states of catalysts according to the XPS analysis.

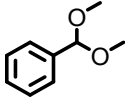
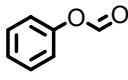
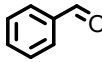
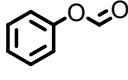
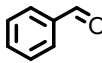
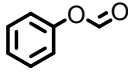
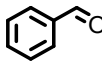
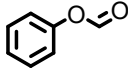
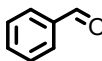
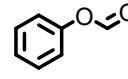
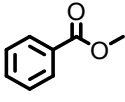
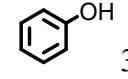
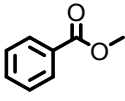
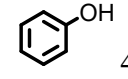
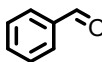
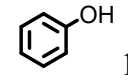
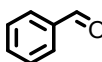
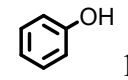
Sample	N=C-N ^a (%)	C-NH ₂ ^a (%)	C-C ^a (%)	C=N-C ^b (%)	C-N-H ^b (%)	N-(C) ₃ ^b (%)	π -excitation ^b (%)
GCN	83.5	4.9	11.7	67.7	23.5	2.9	5.9
P _{1,2} -CN	76.0	9.8	14.2	68.2	18.5	10.4	2.9

^aC 1s states. ^bN 1s states.

Table S3. Catalytic performances of other conventional photocatalysts for the cleavage of C-C bonds in 2-phenoxy-1-phenylethanol (pp-ol). Reaction conditions: 10 mg of photocatalyst, 10 mg of pp-ol, 3 mL of MeOH, 425 nm LED, O₂, 9 h.

Entry	Catalyst	Conversion (%)	Yield of pp-one (%)	Yield of P1 (%)	Yield of P2 (%)
1	V ₂ O ₅	<1	<1	<1	<1
2	In ₂ O ₃	<1	<1	0	0
3	Bi ₂ O ₃	<1	<1	0	0
4	CdS	<1	<1	0	0
5	CuO	0	0	0	0

Table S4. Comparison of performances of PCN catalyst with photo-, thermo-, and electro-catalytic systems for the C-C bond cleavage in pp-ol.

Entry	Catalyst	Conversion (%)	Yield of the main products (%)		References
Photocatalysis					
1	PCN	>99.9	 91	 56	This work
2	porous C ₃ N ₄	99	 65	 31	1
3	mesoporous C ₃ N ₄	96	 51	 30	2
4	PC-Mes ^a	83	 69	 58	3
5	Mo ₁₃₂ , K ₂ S ₂ O ₈	92	 73	 5	4
Thermocatalysis					
6	Pd/CeO ₂	70	 27	 38	5
7	Au-Pd-CTFs	96	 17	 49	6
Electrocatalysis					
8	TCP-Pd/CNTs	99	 32	 18	7
9	Mo@NiCoOOH	93	 57	 13	8

^aPC-MES = Mes-10-phenyl-Acr⁺-BF₄⁻

Supplementary Figures

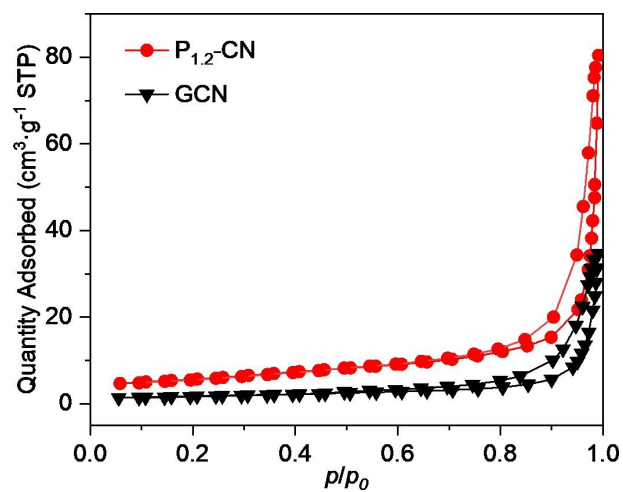


Figure S1. N₂ adsorption-desorption isotherms of the GCN and P_{1.2}-CN catalysts.

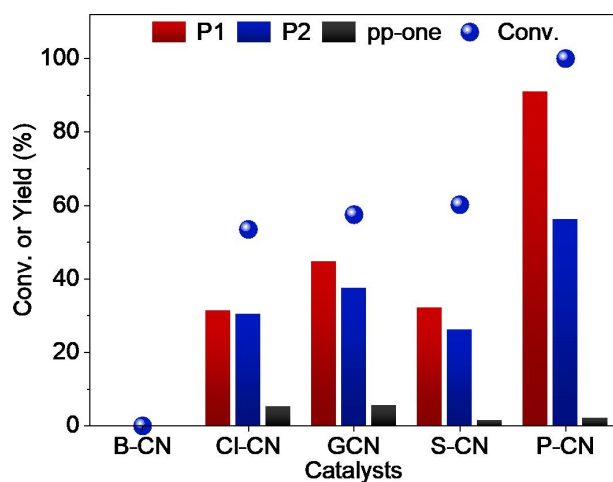


Figure S2. Screening of different dopants for photocatalytic depolymerization of pp-ol. Reaction conditions: 10 mg of pp-ol, 10 mg of catalyst, 3 mL of methanol, O₂, 8 W blue 420 nm LED light, 9 h.

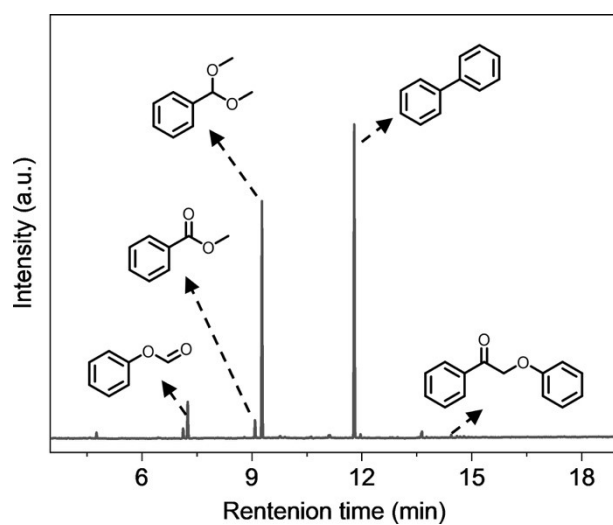


Figure S3. GC-MS spectrum of 2-phenoxy-1-phenylethanol (pp-ol) conversion catalyzed by P_{1,2}-CN for 9 h.

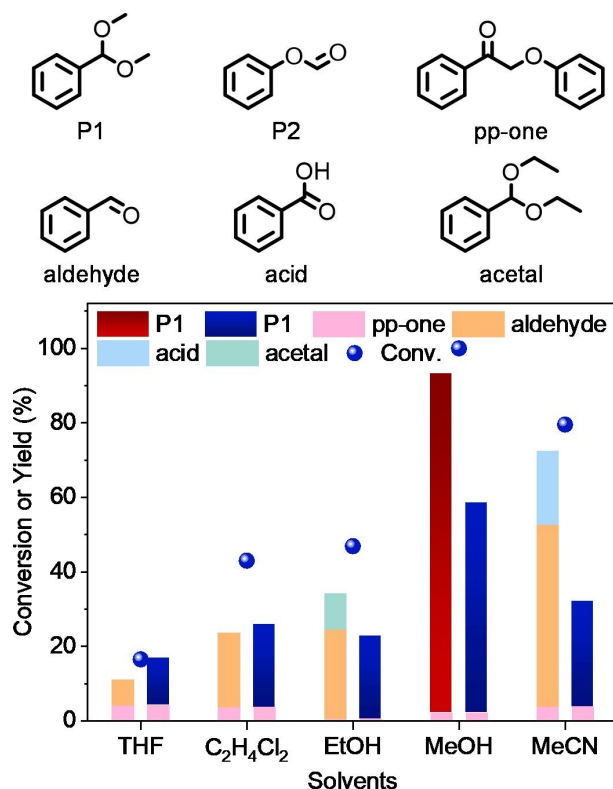


Figure S4. Screening of reaction solvents for photocatalytic depolymerization of pp-ol. Reaction conditions: 10 mg of pp-ol, 10 mg of catalyst, 3 mL of solvent, O₂, 8 W blue 420 nm LED light, 9 h.

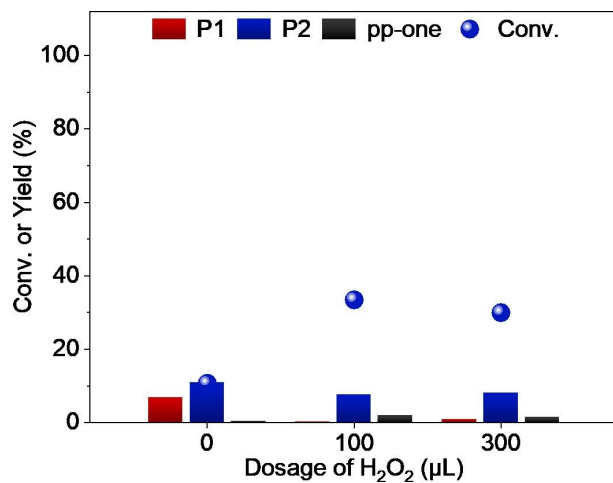


Figure S5. Screening of using H₂O₂ as oxidant for photocatalytic depolymerization of pp-ol. Reaction conditions: 10 mg of pp-ol, 10 mg of catalyst, 3 mL of methanol, N₂, H₂O₂, 8 W blue 420 nm LED light, 9 h.

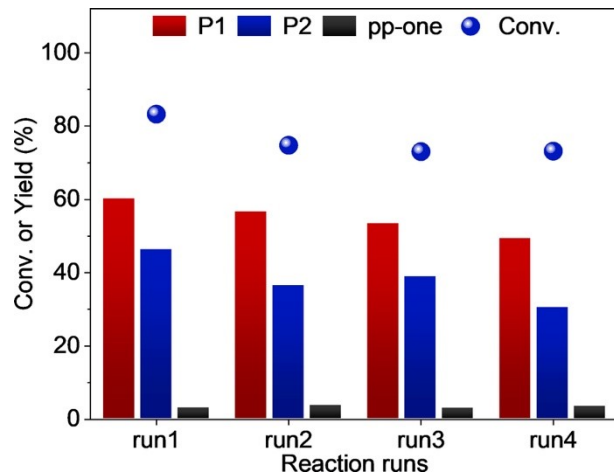


Figure S6. The stability tests of the P_{1,2}-CN catalyst.

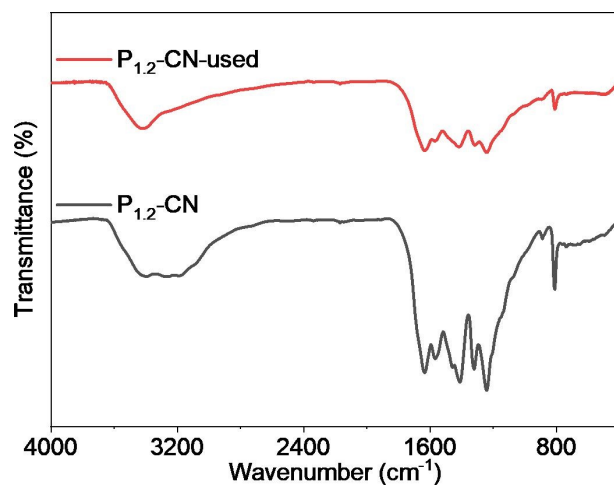


Figure S7. FT-IR spectra of fresh and used P_{1,2}-CN catalysts.

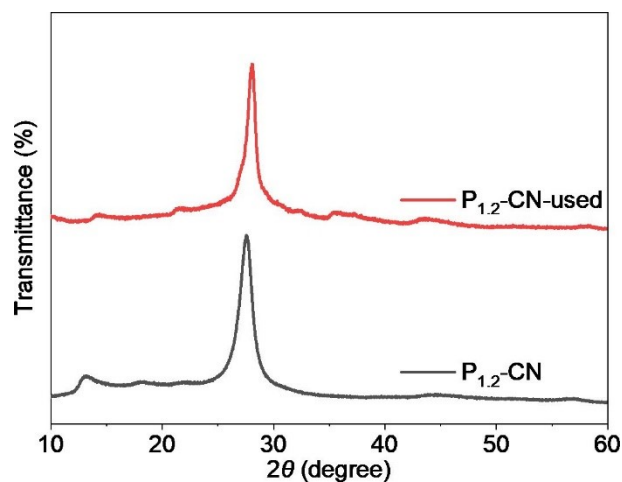


Figure S8. XRD patterns of fresh and used P_{1,2}-CN catalysts.

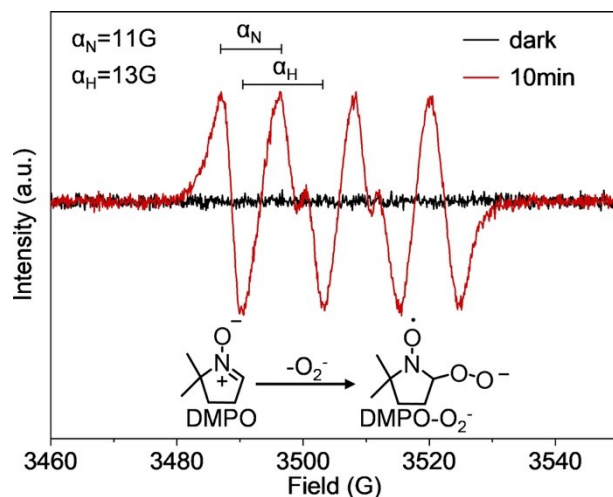


Figure S9. ESR spectra over P_{1,2}-CN in acetonitrile dispersion.

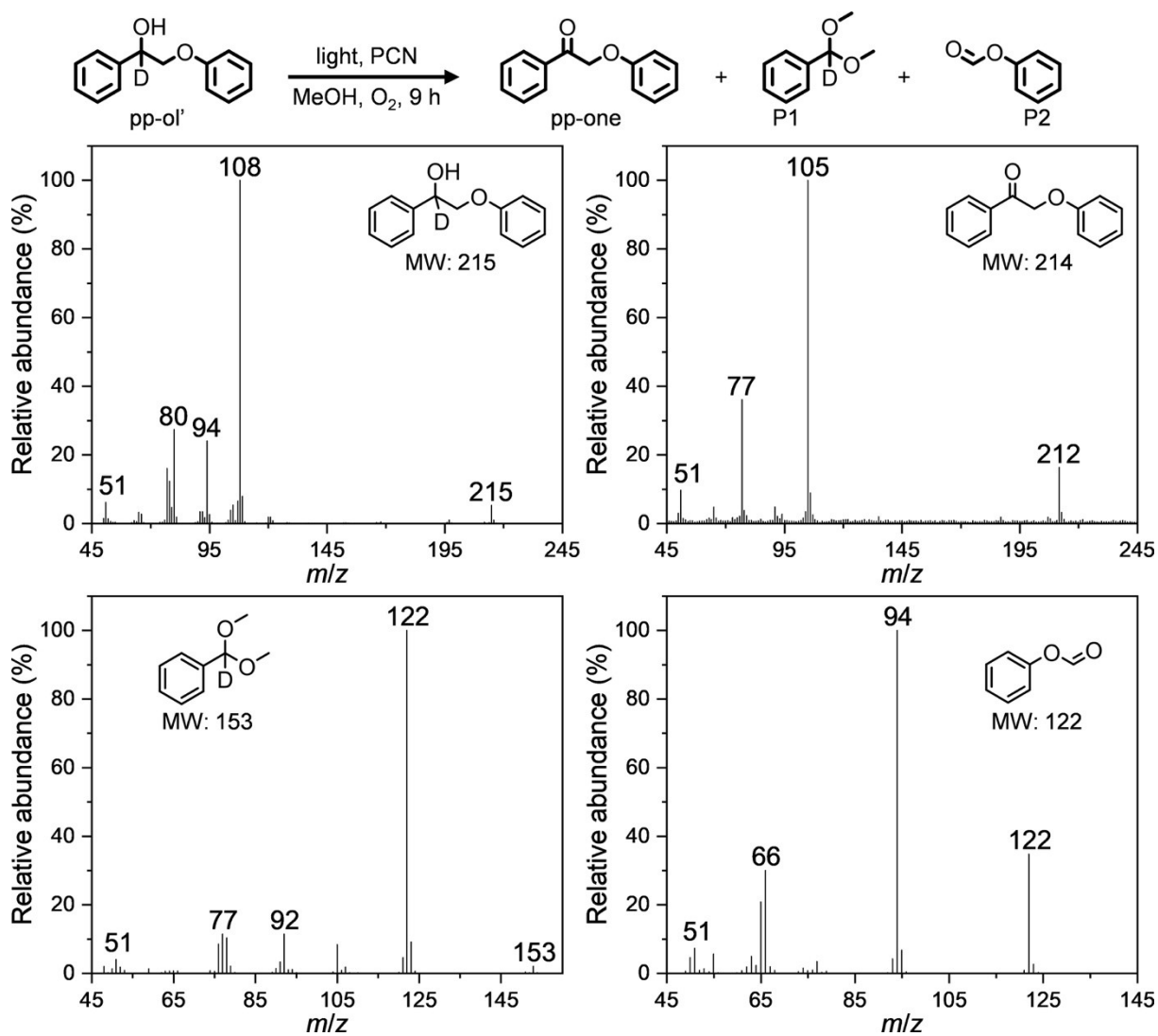


Figure S10. Mass spectra of the reaction system of pp-ol'.

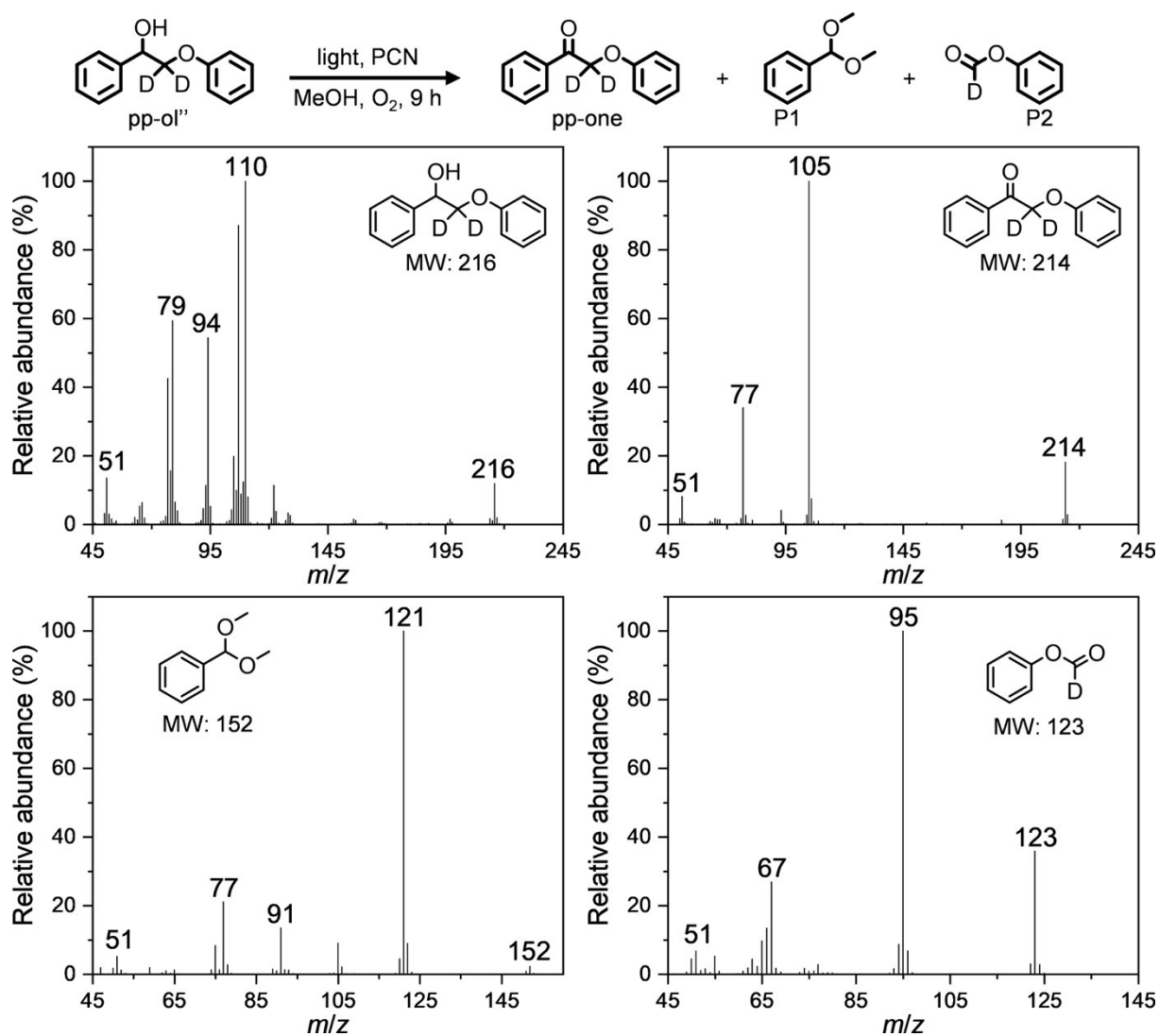


Figure S11. Mass spectra of the reaction system of pp-ol''.

References

1. D. Liang, J. Wu, C. Xie, J. Wen, Y. Lyu, Z. Sofer, J. Zheng and S. Wang, *Appl. Catal. B-Environ.*, 2022, **317**, 121690.
2. H. Liu, H. Li, J. Lu, S. Zeng, M. Wang, N. Luo, S. Xu and F. Wang, *ACS Catal.*, 2018, **8**, 4761-4771.
3. Y. Liu, H. Liu, N. Li and F. Wang, *Appl. Catal. B-Environ.*, 2023, **339**, 123137.
4. H.-J. Lee and E. S. Cho, *ACS Sustain. Chem. Eng.*, 2023, **11**, 7624-7632.
5. W. P. Deng, H. X. Zhang, X. J. Wu, R. S. Li, Q. H. Zhang and Y. Wang, *Green Chem.*, 2015, **17**, 5009-5018.
6. L. Zhao, S. Shi, G. Zhu, M. Liu, J. Gao and J. Xu, *Green Chem.*, 2019, **21**, 6707-6716.
7. P. Ren, L. Shi, Z. Kan, J. Bai, Y. Liu, S. Yang, S. Li and S. Liu, *Catal. Sci. Technol.*, 2024, **14**, 973-979.
8. J. Xu, J. Meng, Y. Hu, Y. Liu, Y. Lou, W. Bai, S. Dou, H. Yu and S. Wang, *Research*, 2023, **6**, 0288.