# **Chemical Synthesis**

### **Supplementary Materials**

One-pot synthesis of carbon dots/hydrochar and visible-light-driven photocatalysts for aerobic oxidative coupling of benzylic amines

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#### **Supplementary Figures**



**Supplementary Figure 1A.** The photocatalytic oxidative coupling of benzylamine performance of CPP-x (x = 500, 600, 700, 800).



**Supplementary Figure 1B.** The XRD patterns of a. carbonized pomelo peel CPP-x (x = 500, 600, 700, 800).



**Supplementary Figure 2.** (A) N<sub>2</sub> sorption isotherms and (B) pore size distribution of PP, CDs/HCPP, and CDs/HCPP-700.



**Supplementary Figure 3.** The XPS spectra of as-prepared materials (A) survey; (B) C 1s; (C) O 1s; (D) N 1s.



Supplementary Figure 4. The FT-IR images of a. CPP-x (x = 500, 600, 700, 800).



Supplementary Figure 5. Raman spectra of CPP-x (x = 500, 600, 700, 800).



Supplementary Figure 6. TGA curves under N<sub>2</sub> for PP, CDs, and CDs/HCPP.



Supplementary Figure 7. SEM images of CPP-700.



Supplementary Figure 8. XRD patterns of CDs/HCPP before and after reaction.



**Supplementary Figure 9.** The UV-vis diffuse reflectance spectra of CPP-x (x = 500, 600, 700, 800)



Supplementary Figure 10. PL emission and UV-vis absorption spectra of CDs/HCPP

dispersed in water.



**Supplementary Figure 11.** PL spectra of CDs at different excitation wavelengths varying from 400 to 500 nm.



**Supplementary Figure 12.** Detection of H<sub>2</sub>O<sub>2</sub> in the filtrate of photocatalytic aerobic oxidative coupling of benzylamine over CDs/HCPP, based on a DPD/POD method.



**Supplementary Figure 13.** The possible reaction route of PCDs/HCPP on photocatalytic oxidative coupling of benzylamine.



**Supplementary Figure 14.** The equivalent electrical circuits applicable to fit the EIS data. The equivalent electrical circuits applicable to fit the EIS data are shown in Supplementary Figure 14. The different electrical elements, i.e., Rs and Rct shown in this model represent the electrolyte resistance and charge transfer resistance respectively. Y0 and n represent CPE (constant phase element) parameters. The Nyquist diameter of the electrode deposited with the CDs/HCPP

Somulo	Dat	<b>D</b> c	CPE		
Sample	KCI	KS	Y0 N	Ν	
CDs/HCPP	10,918 Ω	148.66 Ω	1.9643*10 <sup>-6</sup> S	0.84626	



Supplementary Figure 15. (A-D) MS figures.

## **Supplementary Tables**

Sample	C 1s	Specie	C%	<b>O1s</b>	specie	0%	N 1s	Specie	N%
CDs	284.8	C=C	77.6	531.5	C-0	55.5	399.9	Pyridinic N	84.3
	286.6	С-О	17.2	532.8	C=O	44.5	401.9	Graphitic N	15.7
	288.5	C=O	5.2						
CDs/HCPP	284.7	C=C	67.7	531.1	C-O	17.3	399.8	Pyridinic N	76.4
	286.4	С-О	25.4	532.7	C=O	82.7	401.9	Graphitic N	23.6
	288.1	C=O	6.9						
CDs/HCPP-700	284.7	C=C	75.2	531.8	C-O	46.2	398.5	Iminic N	35.0
	286.2	С-О	17.6	533.6	C=O	53.8	400.7	Pyrrolic N	65.0
	288.5	С=О	7.2						

Supplementary Table 1. Binding energies of the C 1s, O 1s and N 1s regions of CDs, CDs/HCPP and CDs/HCPP-700

Supplementary Table 2. Organic element content of as-prepared materials

Sample	C (%)	H (%)	N (%)	0 (%)	Ash (%)
РР	41.65	6.21	2.37	49.06	0.71
CDs	53.00	5.93	2.45	38.62	0
CDs/HCPP	54.04	5.84	3.29	34.16	2.67
CDs/HCPP-700	72.67	2.23	3.48	17.37	4.25

Entry	Catalysts	Condition	Con./%	Sele./%	Yield./%	Ref.
1	Hydrochar	35 W tungsten-bromine lamp	97.1	99.5		1
	from bamboo	$\lambda > 420$ nm, 29 °C, 0.1 Mpa O2, 32 h				I
2	O-CDs	300W Xe lamp, $\lambda > 420$ nm		-	98	2
		90 °C, 0.1 Mpa O <sub>2</sub> ,12 h	-			
3	Cu2O / CDs	20 W LED, $\lambda > 400 \text{ nm}$	07	98	05	2
		50 °C, 0.1 Mpa O <sub>2</sub> , 8 h	97		93	3
4	C70 fullerene	34 W LED, $\lambda = 470 \text{ nm}$		-	98	4
		35 °C, 0.1 Mpa O <sub>2</sub> , 24 h	-			
5	mpg-C3N4	300W Xe lamp, $\lambda > 400$ nm,	00	99	89	5
		80 °C, 0.5 Mpa O <sub>2</sub> , 3.5 h	90			
6	CDs/HCPP	10W LED, $460 < \lambda < 465 \text{ nm}$		-	99	This
		26 °C, air, 6 h	-			work

Supplementary Table 3. The comparison of photocatalytic oxidation of amines between this work and recently reported similar catalytic systems

#### REFERENCES

1. Ye J., Ni K., Liu J., Chen G., Ikram M., Zhu Y. Oxygen - Rich Carbon Quantum Dots as Catalysts for Selective Oxidation of Amines and Alcohols. *ChemCatChem* 2018; 10: 259-265. [DOI: 10.1002/cctc.201701148]

2. Kumar A., Hamdi A., Coffinier Y., Addad A., Roussel P., Boukherroub R., Jain S.L. Visible light assisted oxidative coupling of benzylamines using heterostructured nanocomposite photocatalyst. *J. Photochem. Photobiol. A* 2018; 356: 457-463. [DOI: 10.1016/j.jphotochem.2018.01.033]

3. Su F., Peng H., Yin H., Luo C., Zhu L., Zhong W., Mao L., Yin D., Biowaste-derived hydrochar microspheres: Realizing metal-free visible-light photocatalytic oxidation of amines. *Journal of Catalysis* 2021; 404: 149-162. [DOI: 10.1016/j.jcat.2021.09.019]

4. Khampuanbut A., Santalelat S., Pankiew A., Channei D., Pornsuwan S., Faungnawakij K., Phanichphant S., Inceesungvorn B., Visible-light-driven WO<sub>3</sub>/BiOBr heterojunction photocatalysts for oxidative coupling of amines to imines: Energy band alignment and mechanistic insight. *J Colloid Interface Sci* 2020; 560: 213-224. [DOI: 10.1016/j.jcis.2019.10.057]

5. Zhang D., Han X., Dong T., Guo X., Song C., Zhao Z., Promoting effect of cyano groups attached on g-C<sub>3</sub>N<sub>4</sub> nanosheets towards molecular oxygen activation for visible light-driven aerobic coupling of amines to imines. *Journal of Catalysis* 2018; 366: 237-244. [DOI: 10.1016/j.jcat.2018.08.018]