Facile Construction of Intramolecular g-CN-PTCDA Donor-Acceptor System for Efficient CO_2 Photoreduction

Jiajia Wei [1,†], Xing Chen [2,†], Xitong Ren [2], Shufang Tian [1,*] and Feng Bai [2,*]

[1] Henan International Joint Laboratory of Medicinal Plants Utilization, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China
[2] Key Laboratory for Special Functional Materials of Ministry of Education, National and Local Joint Engineering Research Center for High-Efficiency Display and Lighting Technology, Collaborative Innovation Center of Nano Functional Materials and Applications, School of Materials Science and Engineering, Henan University, Kaifeng 475004, China
* Correspondence: tianshufang@henu.edu.cn (S.T.); baifengsun@126.com (F.B.)
† These authors contributed equally to this work.

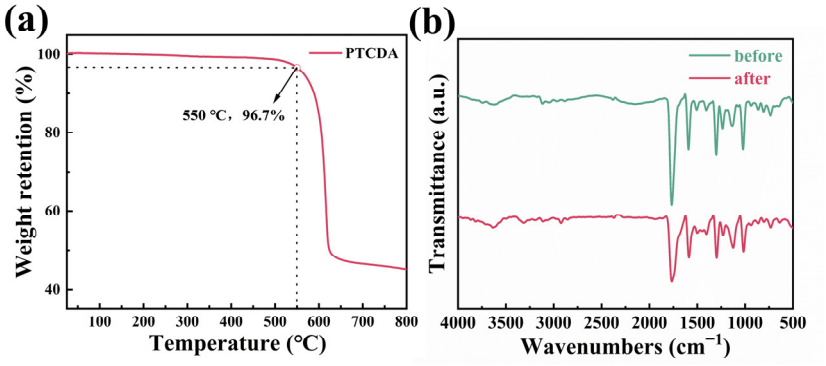

Figure S1 TG (a), and the FT-IR spectra (b) of PTCDA before and after calcination under copolymerization conditions.

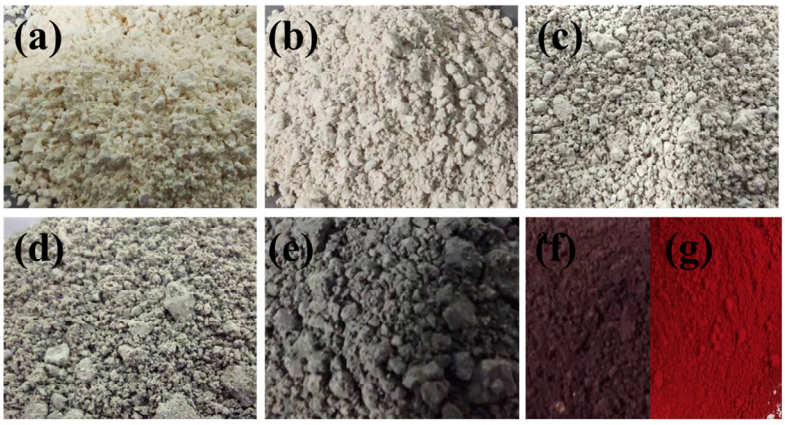

Figure S2 The photographic images of g-CN (a), g-CN-0.5 mg PTCDA (b), g-CN-1 mg PTCDA (c), g-CN-10 mg PTCDA (d), g-CN-100 mg PTCDA (e), g-CN-1 g PTCDA (f), and PTCDA (g).

Table S1 Surface elemental composition of g-CN, g-CN-1 mg PTCDA and g-CN-10 mg PTCDA based on XPS analysis.

Samples	C (Atom %)	N (Atom%)	O (Atom%)	C/N
g-CN	41.31	58.27	0.42	0.71
g-CN-1 mg PTCDA	42.91	55.92	1.16	0.78
g-CN-10 mg PTCDA	46.45	50.27	3.28	0.92

Table S2 The comparison with other DA structure photocatalysts towards CO_2 reduction under visible light.

Catalyst	Donor	Acceptor	Light sources	Solvent	CO evolution rate	Ref.
g-CN-0.01Dbc	Dbc	g-CN	--	H_2O	2.40 μmol g^{-1} h^{-1}	[1]
PY-CN-5	PY	CN	300 W Xe lamp	H_2O	10.3 μmol g^{-1} h^{-1}	[2]
$CNU\text{-}DP_{15.0}$	DP	PCN	300W Xe lamp (>420 nm)	TEOA/H_2O/MeCN (1: 1: 5 v: v: v)	45.4 μmol g^{-1} h^{-1}	[3]
CN–Dbbt-0.01	Dbbt	CN	300 W Xe lamp	H_2O	0.9 μmol g^{-1} h^{-1}	[4]
DA-CTF	DA	CTFs	300 W Xe lamp (>420 nm)	TEOA/ MeCN (1: 2 v: v)	4.7 μmol g^{-1} h^{-1}	[5]
PD-COF-23-Ni	MTAPP	DPP-CHO	300 W Xe	TEOA/H_2O/MeCN (0.5: 2: 3 v: v: v)	40 μmol g^{-1} h^{-1}	[6]
g-CN-Bz (0.01)	Bz	g-CN	300 W Xe lamp	H_2O	0.91 μmol g^{-1} h^{-1}	[7]
g-CN-1 mg PTCDA	PTCDA	g-CN	5 W LED lamp (>420 nm)	TEOA/MeCN (1: 4 v: v)	5.25 μmol g^{-1} h^{-1}	This work
g-CN-1 mg PTCDA-Co	PTCDA	g-CN	5 W LED lamp (>420 nm)	TEOA/MeCN (1: 4 v: v)	87.2 μmol g^{-1} h^{-1}	

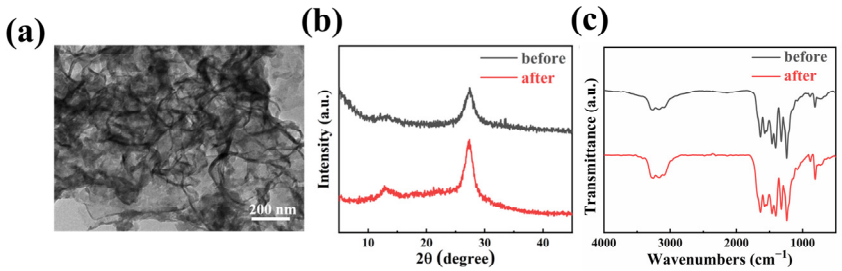

Figure S3 TEM (a), XRD pattern (b), and FT-IR spectra (c) of g-CN-1 mg PTCDA-Co sample before and after four cycles of catalytic reaction.

Table S3 The fitting parameters and average decay time of the time-resolved PL, rate constants of charge separation (k_{ET}) and quantum yield (η_{ET}) for g-CN and g-CN-1 mg PTCDA.

	g-CN	g-CN-1 mg PTCDA
A1	0.7867	0.7809
τ1	1.3524	1.4695
A2	0.2536	0.2430
τ2	7.1001	6.3826
Average life time [ns]	4.97	4.29
$k_{ET}/10^8 s^{-1}$		0.32
η_{ET}/%		13.7

$k_{ET}=(1/\tau_{Ave})_{nanohybrid}-(1/\tau_{Ave})_{g\text{-}CN}$; $\eta_{ET}= [(1/\tau_{Ave})_{nanohybrid} -(1/\tau_{Ave})_{g\text{-}CN}]/(1/\tau_{Ave})_{nanohybrid}$

Table S4 The fitting values for the electrochemical impedance spectroscopy simulation fit for g-CN and g-CN-1 mg PTCDA.

Samples	Rs	Rct (Ω)	CPE_{ct} (μF)
g-CN	25.15	16478	0.94
g-CN-1 mg PTCDA	25.71	9804	0.93

References

1. Song, X.; Zhang, X.; Wang, M.; Li, X.; Zhu, Z.; Huo, P.; Yan, Y. Fabricating Intramolecular Donor-Acceptor System via Covalent Bonding of Carbazole to Carbon Nitride for Excellent Photocatalytic Performance towards CO_2 Conversion. *Journal of Colloid and Interface Science* **2021**, *594*, 550–560.

2. Song, X.; Mao, W.; Wu, Y.; Wang, M.; Liu, X.; Zhou, W.; Huo, P. Fabricating Carbon Nitride-Based 3D/0D Intramolecular Donor-Acceptor Catalysts for Efficient Photoreduction of CO_2. *New J. Chem.* **2022**, *46*, 20225–20234.

3. Hayat, A.; Rahman, M.U.; Khan, I.; Khan, J.; Sohail, M.; Yasmeen, H.; Liu, S.; Qi, K.; Lv, W. Conjugated Electron Donor-Acceptor Hybrid Polymeric Carbon Nitride as a Photocatalyst for CO_2 Reduction. *Molecules* **2019**, *24*, 1779.

4. Zhang, X.; Wang, M.; Song, X.; Yan, Y.; Huo, P.; Yan, Y.; Yang, B. Boosting Charge Carrier Separation Efficiency by Constructing an Intramolecular DA System towards Efficient Photoreduction of CO_2. *New J. Chem.* **2021**, *45*, 6042–6052.

5. Zhong, H.; Hong, Z.; Yang, C.; Li, L.; Xu, Y.; Wang, X.; Wang, R. A Covalent Triazine-Based Framework Consisting of Donor-Acceptor Dyads for Visible-Light-Driven Photocatalytic CO_2 Reduction. *ChemSusChem* **2019**, *12*, 4493–4499.

6. Xu, N.; Diao, Y.; Qin, X.; Xu, Z.; Ke, H.; Zhu, X. Donor-Acceptor Covalent Organic Frameworks of Nickel (II) Porphyrin for Selective and Efficient CO_2 Reduction into CO. *Dalton Trans.* **2020**, *49*, 15587–15591.

7. Zhang, X.; Song, X.; Yan, Y.; Huo, P. Construction of Carbon Nitride Based Intramolecular D-A System for Effective Photocatalytic Reduction of CO_2. *Catal Lett* **2022**, *152*, 559–569.