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N, S co-doped hierarchically porous carbon materials for efficient metal-free catalysis

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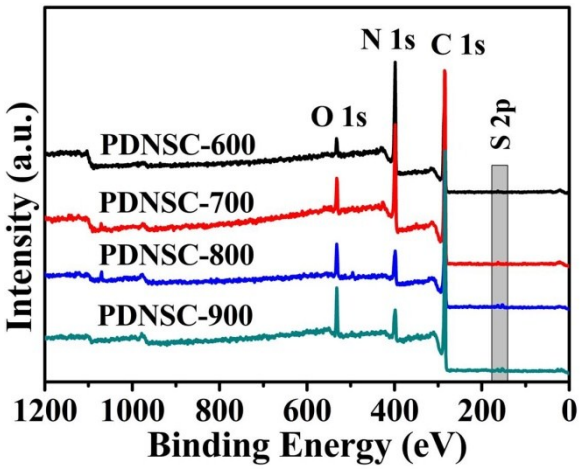


Fig. S1. The wide scan spectra of PDNSC-600, PDNSC-700, PDNSC-800 and PDNSC-900 catalysts.

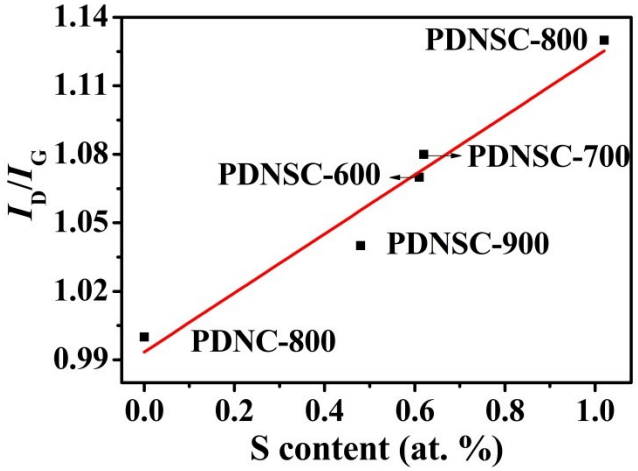


Fig. S2. Linear correlation between the S doping concentration and the values of I_D/I_G in PDNSC-X catalysts.

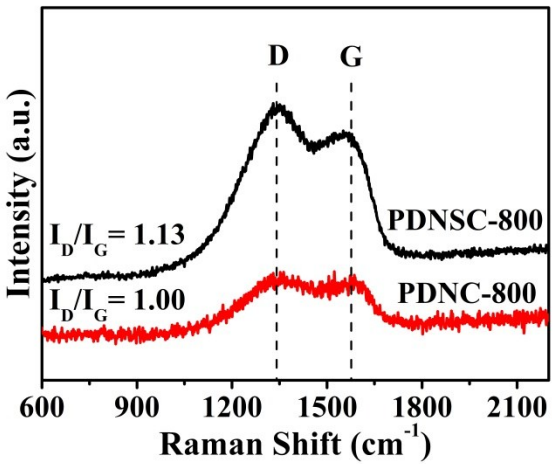


Fig. S3. The comparison between PDNC-800 and PDNSC-800 catalyst in Raman spectra.

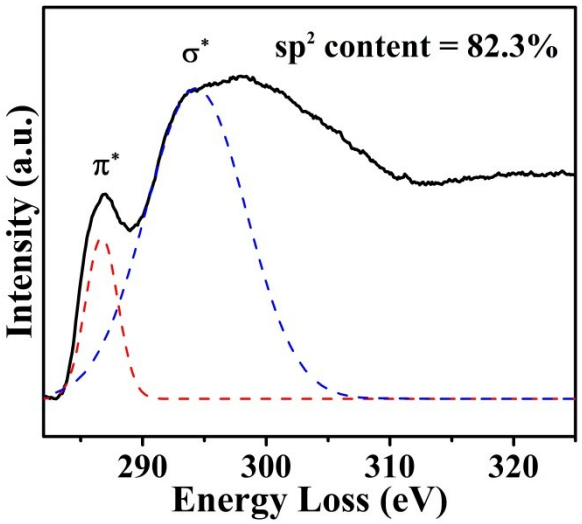


Fig. S4. The EELS C K-edges spectrum of PDNSC-800 catalyst.

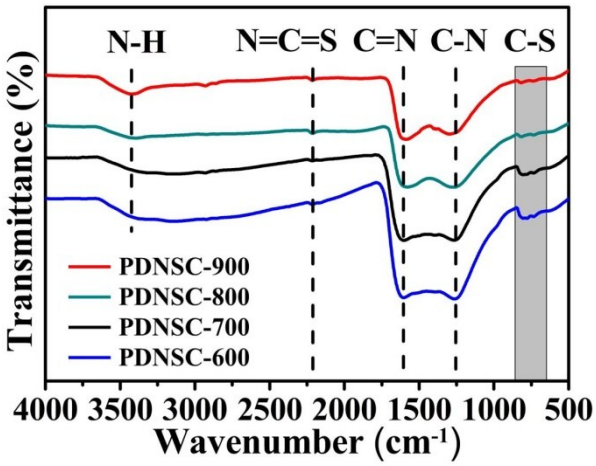


Fig. S5. The FT-IR spectra of PDNSC-600, PDNSC-700, PDNSC-800 and PDNSC-900 catalysts.

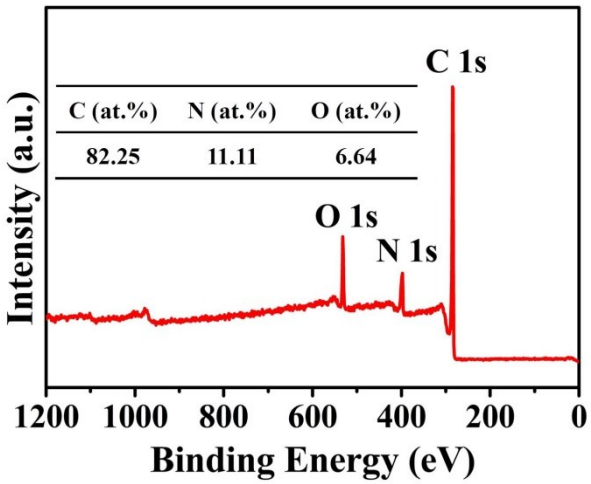


Fig. S6. The wide scan spectra and element contents of PDNC-800 catalyst.

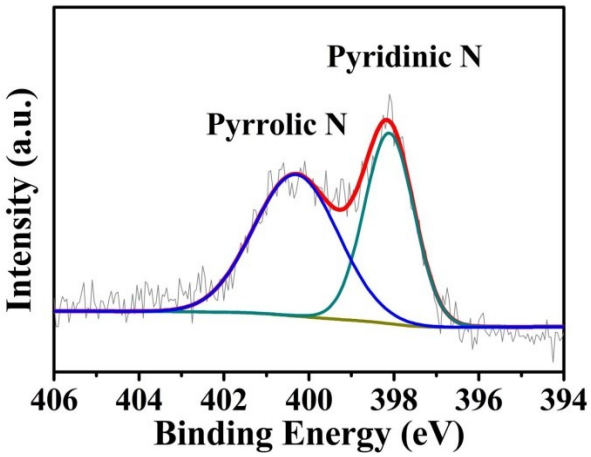


Fig. S7. The N 1s spectra of PDNC-800 catalyst.

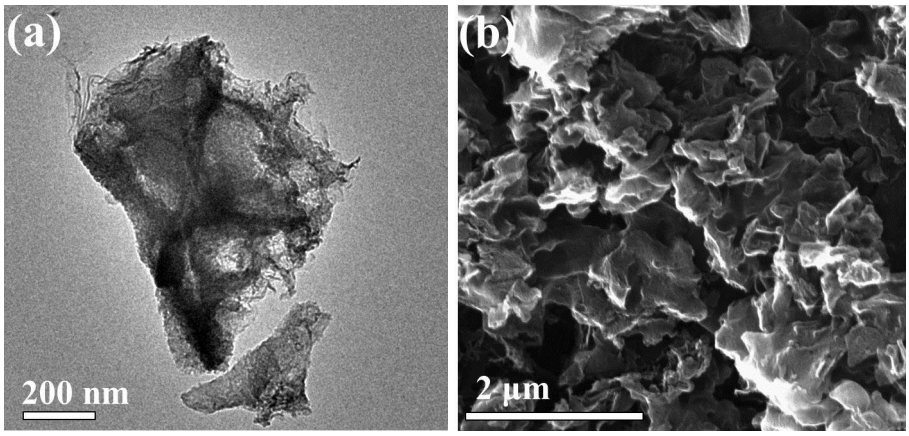


Fig. S8. The TEM image (a) and SEM image (b) of reused PDNSC-800 catalysts.

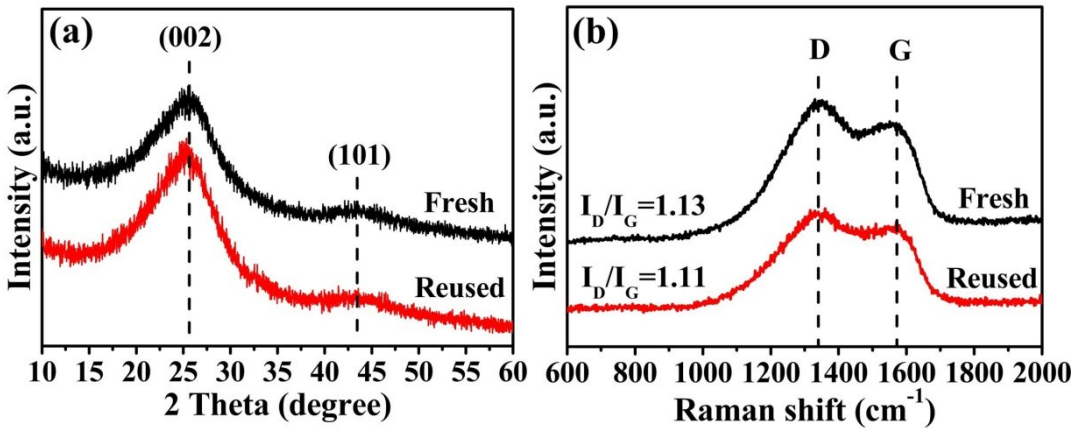


Fig. S9. The comparison between fresh and reused PDNSC-800 catalyst in PXRD patterns (a) and Raman spectra (b).

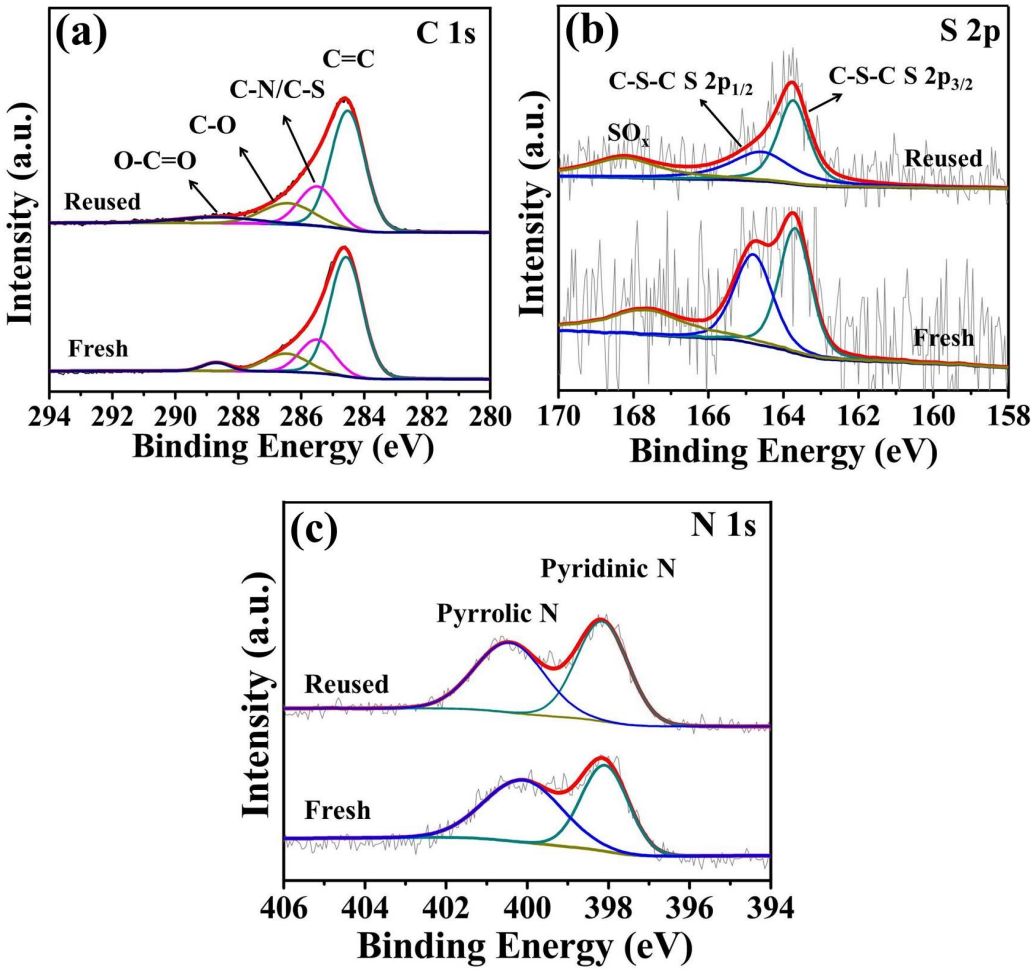


Fig. S10. The comparison between fresh and reused PDNSC-800 catalyst in C 1s spectra (a), S 2p spectra (b) and N 1s spectra (c).

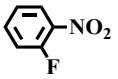
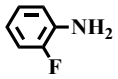
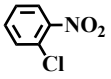
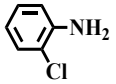
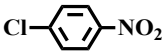
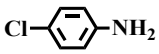
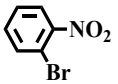
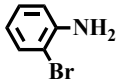
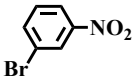
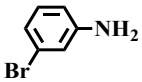
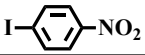
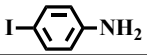
Table S1. Texture parameters of prepared PDNSC-X catalysts and the comparison of catalytic performance in reduction of nitrobenzene.

Entry	Samples	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Average pore size (nm)	TOF ($mol \cdot g^{-1}h^{-1}$)
1	PDNSC-600	18.6	0.030	13.8	2.60×10^{-3}
2	PDNSC-700	211.9	0.18	3.4	9.05×10^{-3}
3	PDNSC-800	351.3	0.32	3.7	1.67×10^{-2}
4	PDNSC-900	495.7	0.38	3.0	1.63×10^{-2}

Table S2. The comparison of catalytic activity of PDNSC-800 catalyst with other reported catalysts in reduction of nitrobenzene.

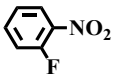
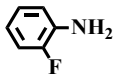
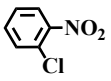
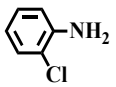
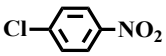
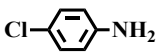
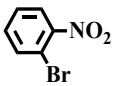
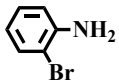
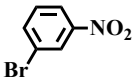
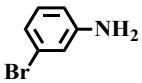
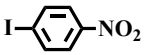
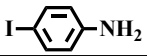
Entry	Catalyst/mg	N_2H_4 (mmol)	Temp. (°C)	Time (h)	TOF ($mol \cdot g^{-1}h^{-1}$)	Ref.
1	NC-700/40	5	100	3.5	3.57×10^{-3}	[1]
2	BNC/10	10	100	8	1.23×10^{-2}	[2]
3	BN-HCS-800/10	17.5	100	1	2.50×10^{-2}	[3]
4	PDNSC-800/30	8.7	100	0.6	2.78×10^{-2}	This work

Table S3. The reduction of different substituted nitroarenes catalyzed by PDNC-800 catalyst under the optimal conditions.[a]

Entry	Substrate	Product	Time (h)	Conv./ Sel. (%)[b]	TOF ($mol \cdot g^{-1}h^{-1}$)
1			0.5	43.8/97.9	1.51×10^{-2}
2			1	57.5/>99	1.61×10^{-2}
3			1	37.9/98.3	1.65×10^{-2}
4			1.5	55.4/>99	1.10×10^{-2}
5			1.5	50.3/>99	1.11×10^{-2}
6			2	37.1/97.2	7.99×10^{-3}

[a] Reaction conditions: 0.5 mmol substrate, 30 mg PDNC-800 catalyst, 3 mL of ethanol, 500 μL $N_2H_4 \cdot H_2O$, 90 °C.

Table S4. The reduction of different substituted nitroarenes catalyzed by SC-800 catalyst under the optimal conditions.[a]

Entry	Substrate	Product	Time (h)	Conv./ Sel. (%)[b]	TOF ($mol \cdot g^{-1}h^{-1}$)
1			0.5	90.3/94.6	1.51×10^{-2}
2			1	97.1/93.3	1.61×10^{-2}
3			1	96.8/92.9	1.65×10^{-2}
4			1.5	94.5/91.8	1.10×10^{-2}
5			1.5	95.3/92.5	1.11×10^{-2}
6			2	92.7/91.0	7.99×10^{-3}

[a] Reaction conditions: 0.5 mmol substrate, 30 mg SC-800 catalyst, 3 mL of ethanol, 500 μL $N_2H_4 \cdot H_2O$, 90 °C.

Table S5. The comparison of element contents in fresh and reused PDNSC-800 catalysts.

Catalyst	C (at.%)	N (at.%)	S (at.%)	O (at.%)
Fresh PDNSC-800	71.98	15.71	1.02	11.29
Reused PDNSC-800	77.38	13.62	0.93	8.07

References

[1] X. Hu, Y. Long, M. Fan, M. Yuan, H. Zhao, J. Ma, Z. Dong, Two-dimensional covalent organic frameworks as self-template derived nitrogen-doped carbon nanosheets for eco-friendly metal-free catalysis, Appl. Catal. B-Environ., 244 (2019) 25-35.

[2] Y. Zhang, Y. Zhai, M. Chu, L. Huo, H. Wang, Y. Gao, Synergistic Effect of B and N Dopants in Catalytic Transfer Hydrogenation, Asian J. Org. Chem., 7 (2018) 1107-1112.

[3] L. Li, L. Li, C. Cui, H. Fan, R. Wang, Heteroatom-doped Carbon Spheres from Hierarchical Hollow Covalent Organic Framework Precursors for Metal-Free Catalysis, ChemSusChem, 10 (2017) 4921-4926.