

Electronic Supplementary Material for
Activating atomically dispersed Co-N/C sites on g-C₃N₄
nanosheets via incorporating sulfur enables efficient visible light
H₂ evolution

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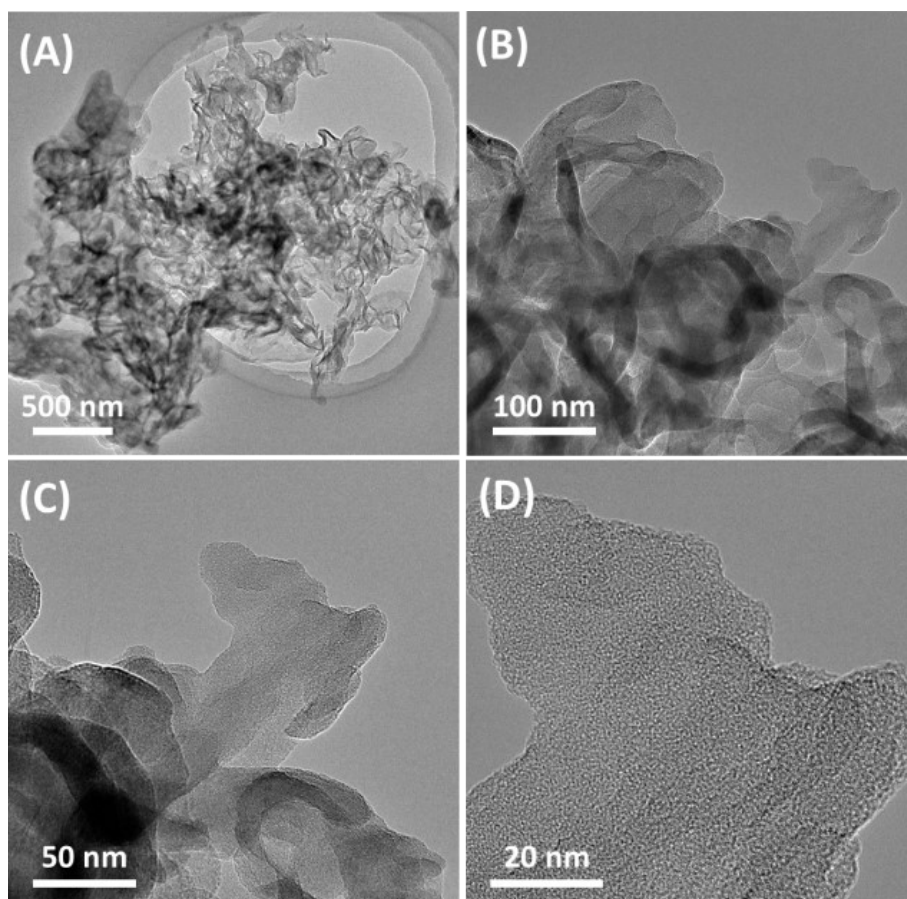


Fig. S1 TEM images of pristine CNs.

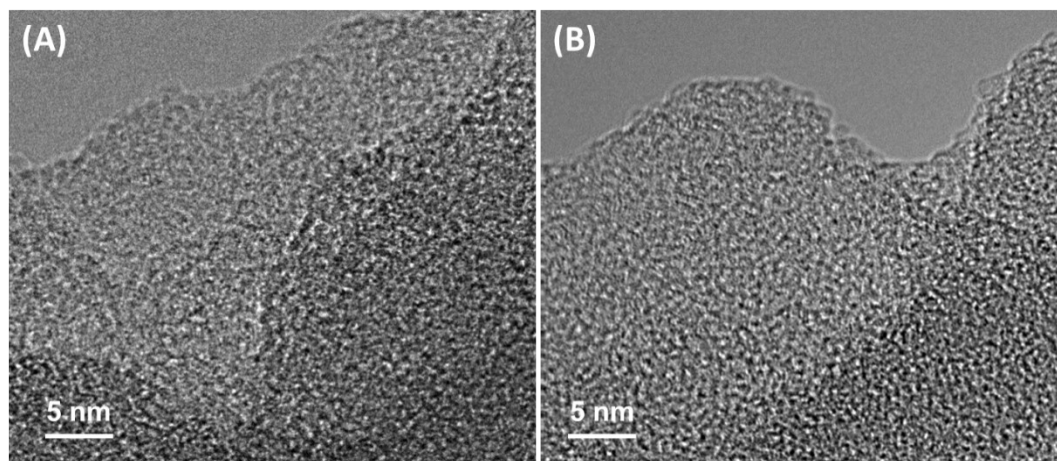


Fig. S2 HRTEM images of (A) Co-CN and (B) S-Co-CN.

Table S1 Chemical composition of Co-CN and S-Co-CN catalysts determined by using EDX analysis.

Sample	C (at.%)	N (at.%)	Co (at.%)	O (at.%)	S (at.%)
Co-CN	41.94	56.03	0.18	1.85	0
S-Co-CN	43.88	50.14	0.17	5.62	0.19

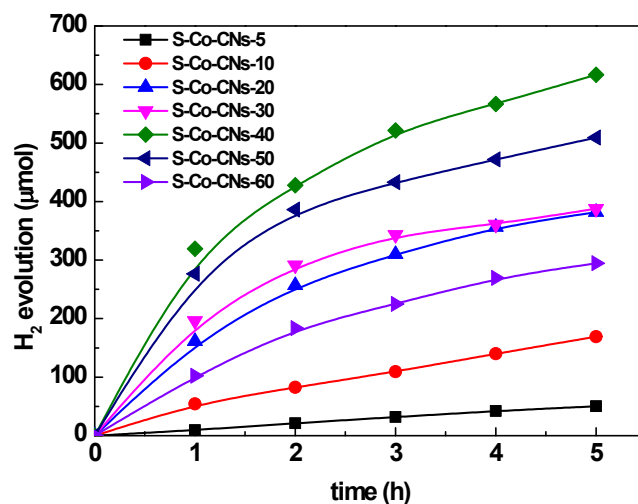


Fig. S3 Time courses of H₂ evolution over ErB-sensitized S-Co-CNs catalysts with different Co contents. Reaction conditions: catalyst, 50 mg; 100 mL of TEOA solution, 10%, pH 8; ErB, 0.2 mM; light source, 30-W LED lamp, $\lambda \geq 450$ nm.

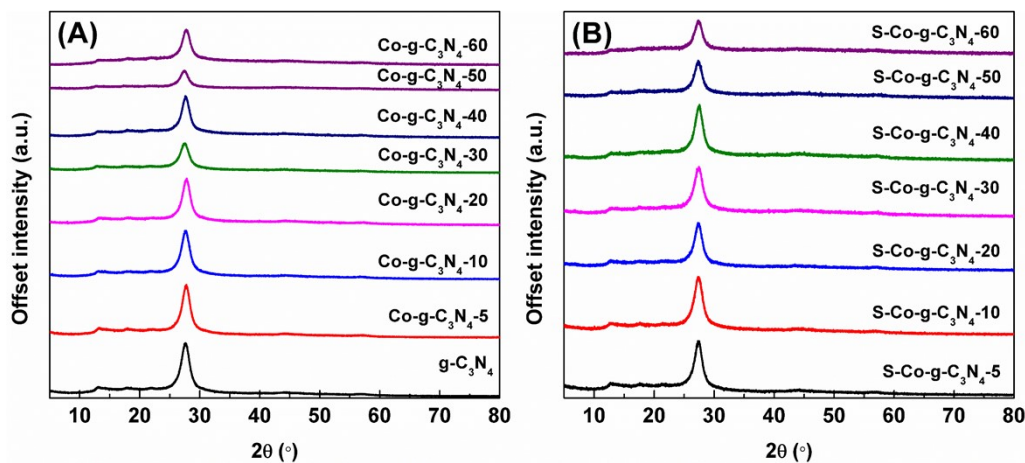


Fig. S4 XRD patterns of (A) Co-g-CNs and (B) S-Co-g-CNs prepared with with different amounts of Co(NO₃)₂·6H₂O.

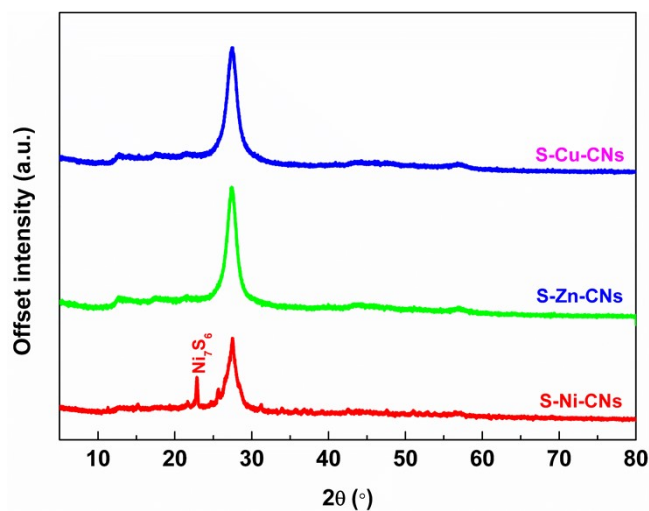


Fig. S5 XRD patterns of S-M-CNs catalysts.

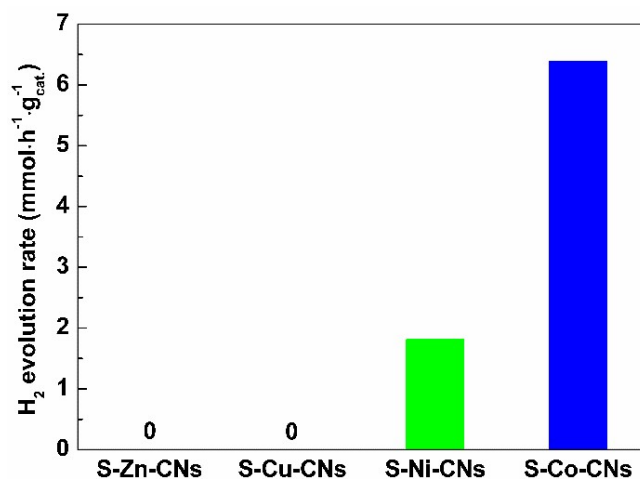


Fig. S6 H₂ evolution rates on different S-M-CN catalysts in ErB-TEOA system.

Reaction conditions: catalyst, 50 mg; 100 mL of TEOA solution, 10%, pH 8; ErB, 0.2 mM; light source, 30-W LED lamp, $\lambda \geq 450$ nm.

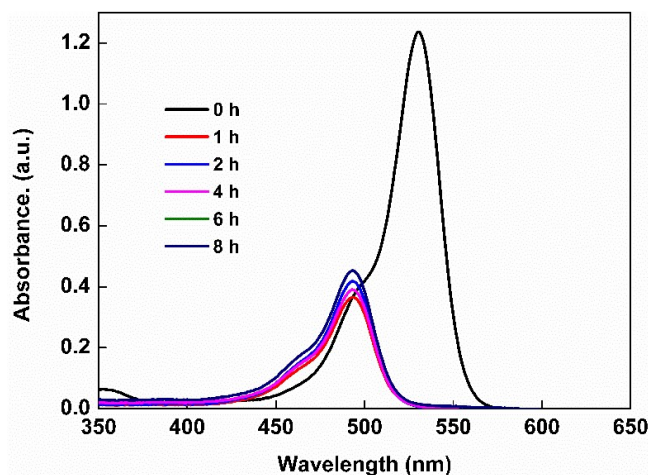


Fig. S7 UV-vis absorption spectra of ErB during the photocatalytic H₂ reaction under visible light irradiation. Reaction conditions: S-Co-CNs, 50 mg; ErB, 0.2 mM; 100 mL TEOA solution, pH 8; light source, 30-W LED lamp, $\lambda \geq 450$ nm. The S-Co-CNs was removed by filtration and the remaining ErB solution was diluted by 10 times.

Table S2 The comparison of photocatalytic H₂ evolution activity and AQY in dye-sensitized g-C₃N₄ loaded with different cocatalysts under visible light irradiation.

Catalyst	Dye	Reaction conditions	Light source	Activity ($\mu\text{mol h}^{-1}$)	AQY (%)	ref
mpg-C ₃ N ₄ /Pt (1 wt.%) (30 mg)	EY (0.4 M)	TEOA (80 mL, 15 vol.%, pH 7)	250 W high pressure Hg lamp (≥ 420 nm)	115.5	14.4% (520 nm)	1
g-C ₃ N ₄ /Pt (7 wt.%) (100 mg)	EY (12.5 μM)	TEOA (80 mL, 0.79 M, pH 7)	400 W high pressure Hg lamp (≥ 420 nm)	160	18.8 (400~700)	2

g-C ₃ N ₄ /Pt (1.25 wt.%) (100 mg)	ErB (2.27 mM)	TEOA (100 mL, 5 vol.%, pH 9)	300 W Xe lamp (≥ 420 nm)	652.5	33.4% (460 nm)	3
Pt (1 wt. %)/g-C ₃ N ₄ (10 mg)	Zn-tri-PcNc (5.0 $\mu\text{mol g}^{-1}$)	AA (10 mL, 50 mM, pH 1.5–1.8)	300 W Xe lamp (≥ 500 nm)	125.2	1.85% (700 nm)	9
Pt (0.5 wt. %)/g-C ₃ N ₄ (10 mg)	LI-4/Zn-tri-PcNc (5.0 $\mu\text{mol g}^{-1}$)	AA (10 mL, 50 mM, pH 1.5)	300 W Xe lamp (≥ 420 nm)	371.4	7.7% (500 nm)	10
MoS _x (0.5 wt. %)-g-C ₃ N ₄ (100 mg)	ErB (12.5 μM)	TEOA (80 mL, 0.79 M, pH 7)	400 W high pressure Hg lamp (≥ 420 nm)	26	8.3% (545 nm)	8
Co(OH) ₂ (23 wt. %)/g-C ₃ N ₄ (26 mg)	EY/RB (17 mg/25 mg)	TEOA (100 mL, 10 vol.%, pH 10)	300 W Xe lamp (≥ 420 nm)	144.2	29.6% (520 nm); 27.3% (550 nm)	11
g-C ₃ N ₄ /Pt SAs (0.74 wt. %) (10 mg)	EY (0.4 mM)	TEOA (100 mL, 10 vol.%, pH 7)	30 W LED (520 nm)	34.2	0.84% (520 nm)	4
g-C ₃ N ₄ /Pt/GO (50mg)	EY (50 mg)	TEOA (100 mL, 20 vol.%, pH 7)	300 W Xe lamp (≥ 420 nm)	191	9.7% (420nm)	6
PtNi (0.5 wt. %)/g-C ₃ N ₄ (50 mg)	EY (50 mg)	TEOA (100 mL, 20 vol.%, pH 7)	300 W Xe lamp (≥ 420 nm)	294.5	NA	12
MMT/g-C ₃ N ₄ /NiCoP (15 wt. %) (10mg)	EY(0.1mM)	TEOA (100 mL, 10 vol.%, pH 11)	300 W Xe lamp (≥ 420 nm)	125	40.3% (420nm)	7
SnIn ₄ S ₈ /g-C ₃ N ₄ (11 wt. %) (50mg)	CoPc (1.75 mg)	TEOA (100 mL, 15 vol.%)	500 W Xe lamp (≥ 430 nm)	636.99	NA	5
MoS ₂ (50 wt. %)/g-C ₃ N ₄ (5 mg)	EY (20 μM)	TEOA (40 mL, 10 vol.%)	300 W Xe lamp (≥ 420 nm)	8.9	NA	13
S-Co-CNs (0.18 at.% Co, 50 mg,)	ErB (0.2 mM)	TEOA (100 mL, 10 vol.%, pH 8)	30 W LED (≥ 450 nm)	319	13.02% (520 nm)	This work

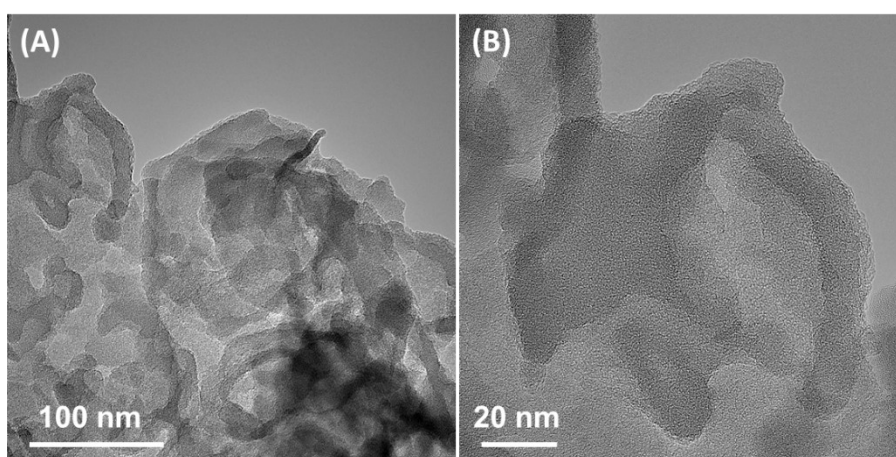


Fig. S8 TEM images of S-Co-CNs catalyst after stability test.

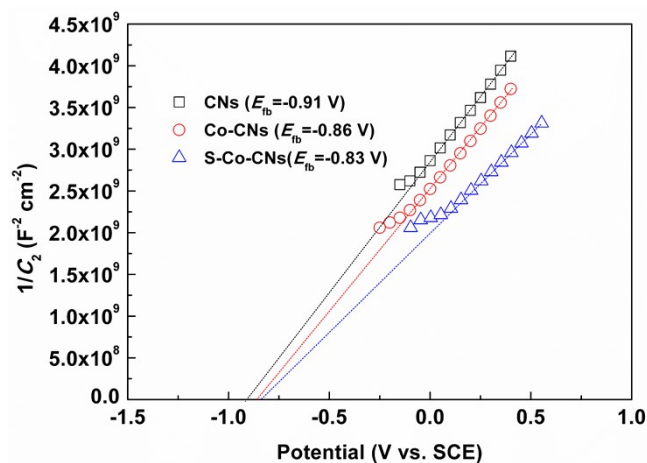


Fig. S9 Mott-Schottky plots of pristine CNs, Co-CNs, and S-Co-CNs.

References

1. S. Min and G. Lu, *J. Phys. Chem. C* 2012, **116**, 19644.
2. J. Xu, Y. Li, S. Peng, G. Lu and S. Li, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7657.
3. Y. Wang, J. Hong, W. Zhang and R. Xu, *Catal. Sci. Technol.*, 2013, **3**, 1703.
4. X. Zhang, L. Yu, C. Zhuang, T. Peng, R. Li and X. Li, *ACS Catal.*, 2014, **4**, 162.
5. X. Zhang, T. Peng, L. Yu, R. Li, Q. Li and Zhen Li, *ACS Catal.*, 2015, **5**, 504.
6. J. Xu, Y. Li and S. Peng, *Int. J. Hydrogen Energy*, 2015, **40**, 353.
7. Z. Li, Y. Wu and G. Lu, *Appl. Catal., B*, 2016, **188**, 56.
8. Y. Xue, Y. Lei, X. Liu, Y. Li, W. Deng, F. Wang and S. Min, *New J. Chem.*, 2018, **42**, 14083.
9. P. Wang, Z. Guan and Q. Li, *J. Mater. Sci.*, 2018, **53**, 774.
10. P. Wang, L. Zong, Z. Guan, Q. Li and J. Yang, *Nanoscale Res. Lett.*, 2018, **13**, 33.
11. J. Xu, Y. Qi, W. Wang and L. Wang, *Int. J. Hydrogen Energy*, 2019, **44**, 4114.
12. M. Lu, Z. Sun, Y. Zhang, Q. Liang, M. Zhou, S. Xu and Z. Li, *Synth. Met.*, 2020, 268, 116480.
13. C. M. Nagaraja, M. Kaur and S. Dhingra, *Int. J. Hydrogen Energy*, 2020, **45**, 8497.