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Electronic Supplementary Information (ESI)

Boosted Photocatalytic Performance on Molecule/Semiconductor Hybrid Materials: Conversion of Sunlight Energy into Hydrogen Fuel

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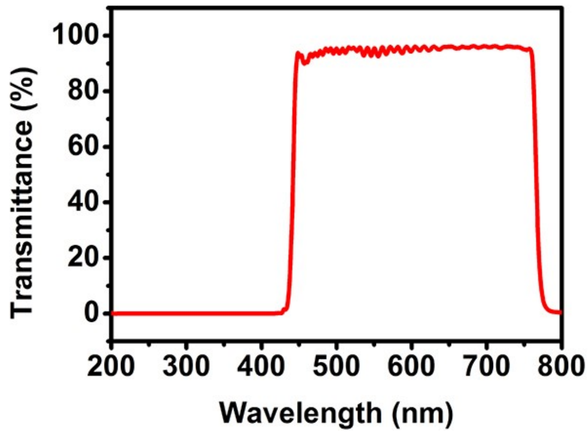

Fig. S1 Transmission spectra of a 420 nm cut-off filter used for photocatalytic measurements.

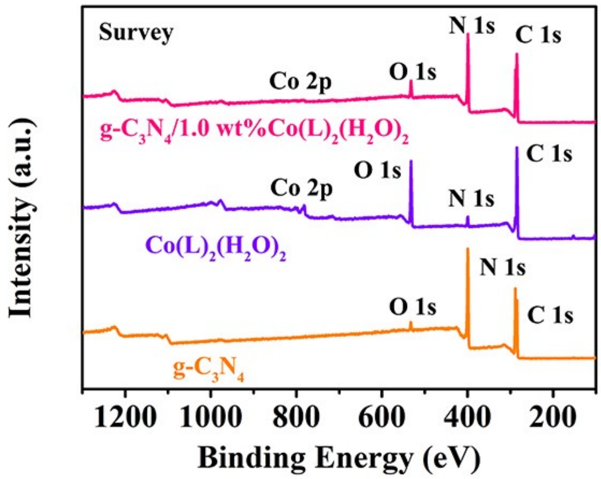

Fig. S2 XPS survey spectra of $g\text{-}C_3N_4$, $Co(L)_2(H_2O)_2$ and $g\text{-}C_3N_4/1.0$ wt%$Co(L)_2(H_2O)_2$.

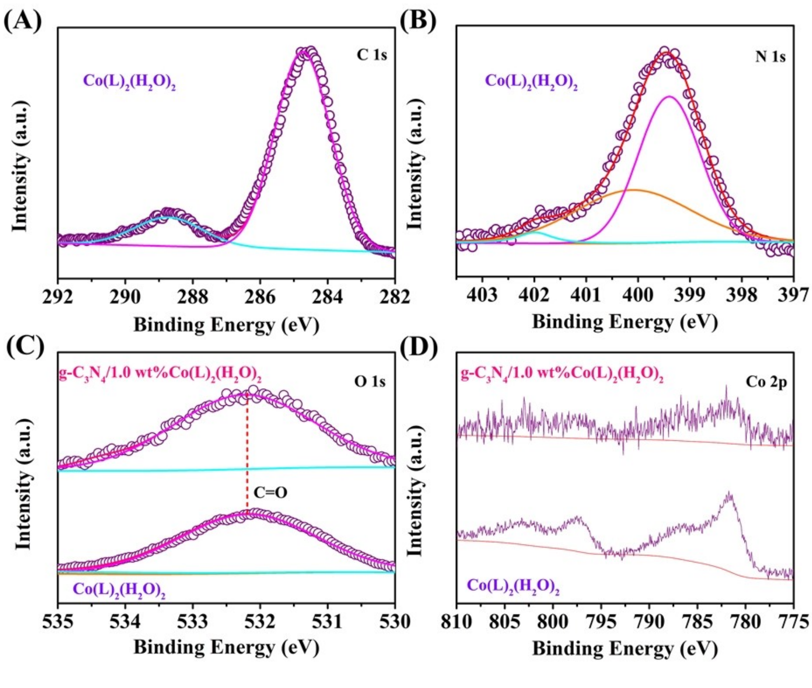

Fig. S3 (A-B) The high-resolution C 1s, N 1s in $Co(L)_2(H_2O)_2$; (C-D) the high-resolution O 1s, Co 2p in $Co(L)_2(H_2O)_2$, $g\text{-}C_3N_4/1.0$ wt%$Co(L)_2(H_2O)_2$.

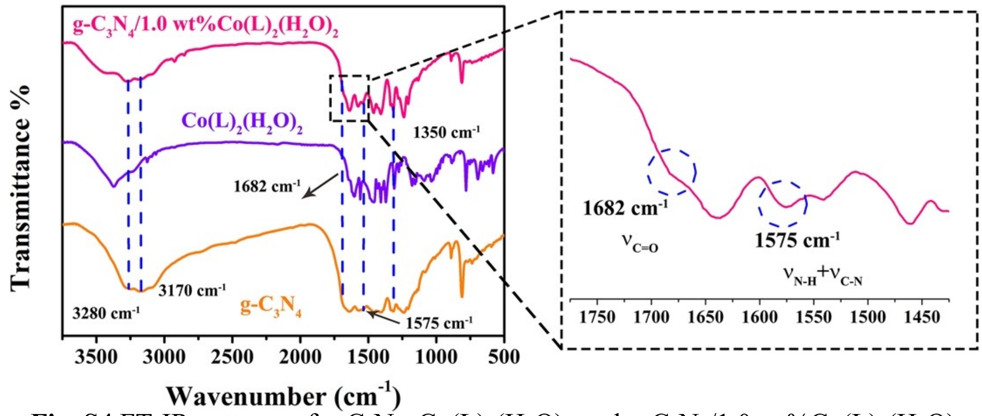

Fig. S4 FT-IR patterns of g-C_3N_4, $Co(L)_2(H_2O)_2$ and g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$.

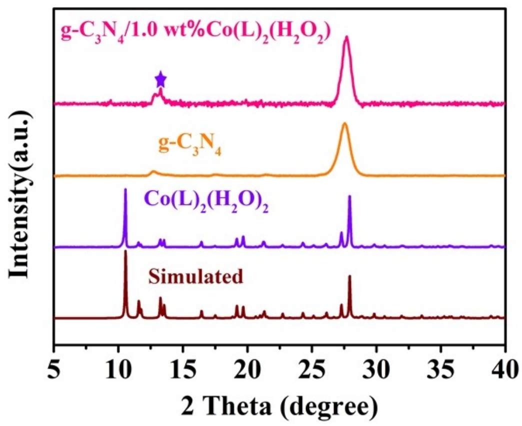

Fig. S5 XRD patterns of g-C_3N_4, $Co(L)_2(H_2O)_2$ and g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$.

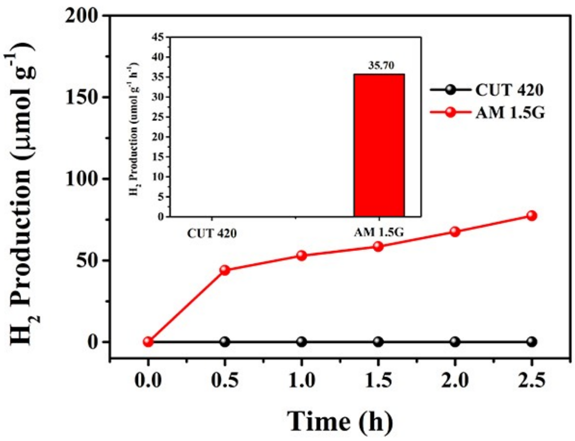

Fig S6. Photocatalytic H_2 production of the $Co(L)_2(H_2O)_2$ under different filters.

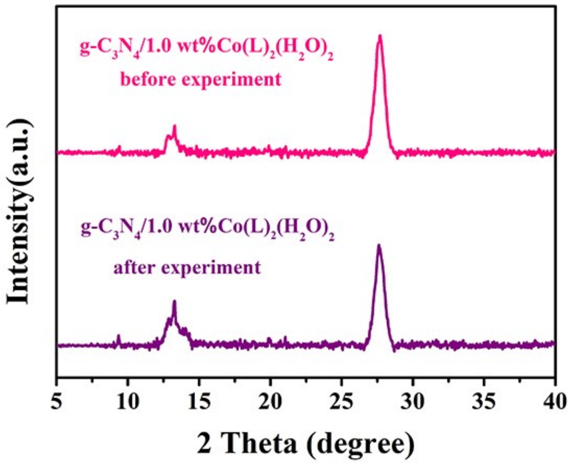

Fig. S7 XRD patterns of g-C_3N_4/1.0 wt%Co(L)$_2$(H_2O)$_2$ sample before and after experiment.

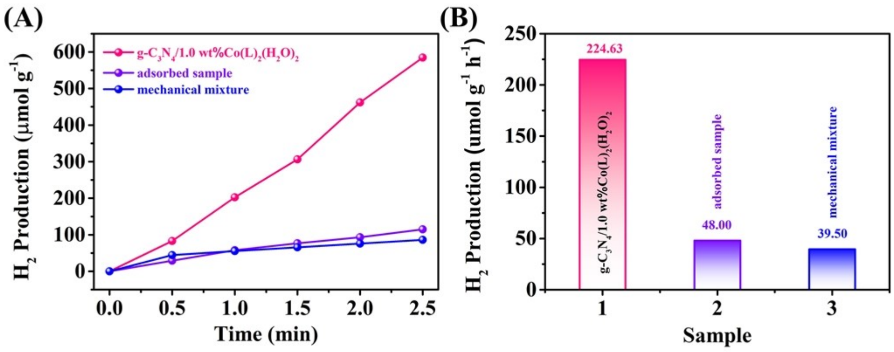

Fig S8. (A-B) Photocatalytic H_2 production with g-C_3N_4/1.0 wt%Co(L)$_2$(H_2O)$_2$, adsorbed sample and mechanical mixture of g-C_3N_4 and Co(L)$_2$(H_2O)$_2$ under the same condition.

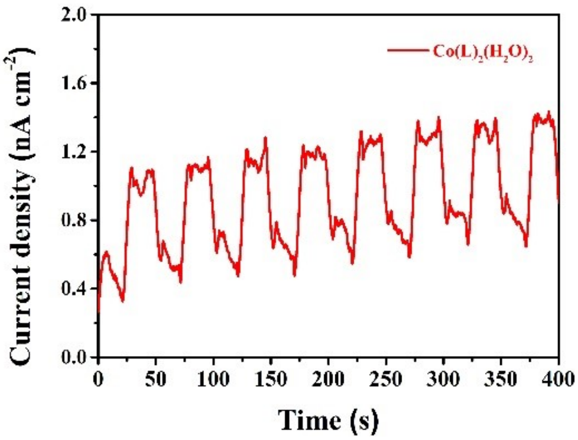

Fig. S9 Transient photocurrent density response of Co(L)$_2$(H_2O)$_2$ under visible light irradiation (λ > 420 nm).

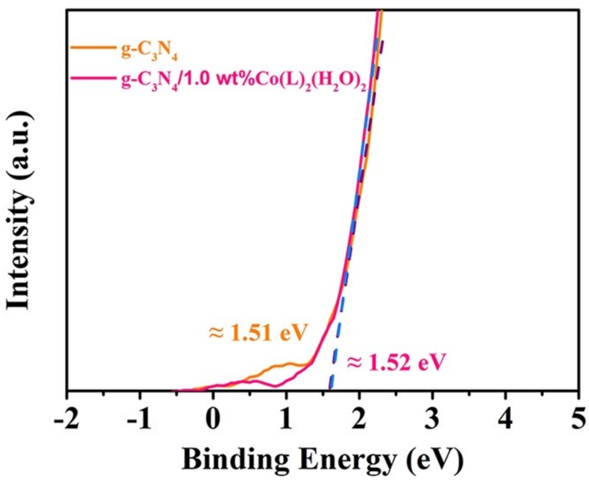

Fig. S10 Valence-band XPS spectra of g-C_3N_4 and g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$.

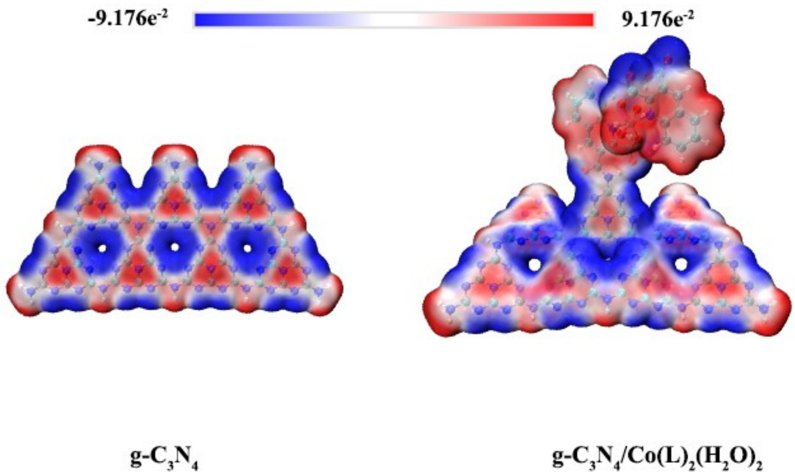

Fig S11. Electrostatic potential (ESP) map of g-C_3N_4 and g-C_3N_4/$Co(L)_2(H_2O)_2$ model. The blue and red color surface corresponds to electron-rich and electron-poor, respectively.

Table S1. Details of reagents and corresponding amounts for preparation of g-C_3N_4/ $Co(L)_2(H_2O)_2$

g-C_3N_4/x wt%$Co(L)_2(H_2O)_2$	g-C_3N_4	$Co(NO_3)_2 \cdot 6H_2O$	L	EDC	HOBt
g-C_3N_4	300 mg	0	0	0	0
g-C_3N_4/0.5 wt%$Co(L)_2(H_2O)_2$	298.5 mg	4 μmol 1.164 mg	4 μmol, 0.868 mg	8 μmol, 1.242 mg	8 μmol, 1.081 mg
g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$	297 mg	8 μmol, 2.328 mg	8 μmol, 1.737 mg	16 μmol, 2.484 mg	16 μmol, 2.162 mg
g-C_3N_4/2.0 wt%$Co(L)_2(H_2O)_2$	294 mg	16 μmol, 4.657 mg	16 μmol, 3.475 mg	32 μmol, 4.968 mg	32 μmol, 4.324 mg
g-C_3N_4/3.0 wt%$Co(L)_2(H_2O)_2$	291 mg	24 μmol, 6.985 mg	24 μmol, 5.212 mg	48 μmol, 7.452 mg	48 μmol, 6.486 mg
$Co(L)_2(H_2O)_2$	0	0.8 mmol, 232.9 mg	0.8 mmol, 217.8 mg	0	0

Table. S2 Cobalt elemental contents in g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$ by ICP-OES.

Sample	Cobalt dosage (wt%)	Cobalt contents (wt%)
g-C_3N_4/1.0 wt%$Co(L)_2(H_2O)_2$	0.78	0.15

Table S3: The comparison of the hydrogen evolution rates between this system and other similar reported work

Photocatalysts	Dosage (mg)	Light source	Sacrificial agents	H_2 evolution rate (μmol·h^{-1})	Ref.
$Co(dcbpy)_2(NCS)_2$/ CQDs/CN	50	300 W Xe lamp (λ > 420 nm)	TEOA	295.9	1
Co@NC/g-C_3N_4	25	300 W Xe lamp (simulated sunlight)	TEOA	161	2
Co-mCN	10	White light-emitting diode (420 < λ > 700 nm)	-	182	3
$[Co(bpy)_3^{2+}]$/BINA-PCN	50	300 W Xe lamp (λ > 420 nm)	TEOA	162	4
Co-CN (3 wt% Pt)	50	300 W Xe lamp (λ > 420 nm)	TEOA	560	5
CoP/g-C_3N_4	2	300 W Xe lamp (λ = 400 nm)	TEOA	195	6
10%Co/CAN (3 wt% Pt)	25	300 W Xe lamp (λ > 420 nm)	TEOA	472.2	7
CNNS-Co (1.0%) (3 wt% Pt)	50	300 W Xe lamp (λ > 420 nm)	TEOA	808.92	8
35% $Co_3(PO_4)_2$/g-C_3N_4	50	Xe lamp (λ > 400 nm)	-	375.6	9
CoS_X/g-C_3N_4	50	350 W Xe lamp (λ > 400 nm)	TEOA	629	10
g-C_3N_4/$Co(L)_2(H_2O)_2$	50	300 W Xe lamp (λ > 420 nm)	TEOA	224.6	This work

Table. S4 Theoretical bandgap, HOMO, LUMO and E_{VB} of g-C_3N_4 and g-C_3N_4/Co(L)$_2$(H_2O)$_2$ according to calculation results of constructed models.

Model	HOMO (eV)	LUMO (eV)	Bandgap (eV)	E_{VB} (eV)
g-C_3N_4	-6.01	-3.34	2.67	1.51
g-C_3N_4/Co(L)$_2$(H_2O)$_2$	-6.02	-4.04	1.98	1.52

Reference

1. Y. Zhang and W. D. Zhang, *Carbon*, 2019, **145**, 488-500
2. Y. Li, S. Zhu, X. Kong, Y. Liang and Z. Cui, *Environmental Research*, 2021, **197**, 111002.
3. B. Yd, Z. A. Cheng, A. Mz, A. Yf, A. Hw, C. Cs, H. A. Hui, L. A. Yang and A. Zk, *Applied Surface Science*, 2020, **509**, 144706.
4. Z. Pan, P. Niu, M. Liu, G. Zhang and X. Wang, *ChemSusChem*, 2020, **13**, 888-892.
5. P. W. Chen, K. Li, Y. X. Yu and W. D. Zhang, *Applied Surface Science*, 2017, **392**, 608-615.
6. Z. Sun, M. Zhu, X. Lv, Y. Liu, C. Shi, Y. Dai, A. Wang and T. Majima, *Applied Catalysis B: Environmental*, 2019, **246**, 330-336.
7. T. A. Zhen, Y. A. Xi, A. Yc, H. A. Hao, H. Jie and A. Bw, *International Journal of Hydrogen Energy*, 2020, **45**, 24792-24806.
8. Y. A. Xi, T. A. Zhen, A. Yc, H. A. Hao, H. Jie and A. Bw, *Journal of Alloys and Compounds*, 2021, **859**, 157754.
9. A. Ws, C. Ml, C. Xh, C. Hr, Y. A. Chao and G. B. Feng, *Chemical Engineering Journal*, 2020, **382**, 122960.
10. J. Fu, C. Bie, B. Cheng, C. Jiang and J. Yu, *Acs Sustainable Chemistry & Engineering*, 2018, **6**, 2767-2779.