Boosting photocatalytic H_2 evolution on g-C_3N_4 via covalent organic frameworks (COFs) modifying

Maolan Luo, Qing Yang, Kewei Liu, Hongmei Cao, Hongjian Yan*

College of Chemistry, Sichuan University, Chengdu, Sichuan, 610065, China
No. 24 South Section 1, Yihuan Road, Chengdu, P. R. China.
E-mail: hjyan@scu.edu.cn; Tel: +86 1355-1341-892

Experimental Section.

Materials

1,3,5-Triformylphloroglucinol (TP) and 4,4',4"-(1,3,5-triazine-2,4,6-triyl) trianiline (TTA) were purchased from Alpha Chemical Co. Ltd. (Zhengzhou, China). Pluronic P123 was obtained from Aldrich. Dimethyl sulfoxide (DMSO), triethanolamine, melamine, sulfuric acid, and methanol were purchased from Kelong Chemistry Reagent Co. Ltd. (Chengdu, China). All chemicals were used as received without any further purification.

Synthesis of g-C_3N_4

g-C_3N_4 was synthesized according to our previous work.[1] Pluronic P123 (5.0 g) and melamine (25.0 g) were dissolved in deionized water (500 mL) at 100 ^oC with magnetic stirring. After 1 hour, 10 mL sulfuric acid solution (H_2SO_4:H_2O =1:1 in volume) was slowly added to the solution, and a white precipitant was obtained. After cooled down to room temperature, the white precipitant was collected by filtration and dried at 80 ^oC for 12 hours. The obtained powder was putted into a quartz tube and then heated to 380 ^oC in 5 minutes, followed by heating to 600 ^oC at a heating rate of 1 ^oC min^{-1}, and maintained at 600 °C for 4 h in the flow of Ar gas. After cooled down to room temperature in the flow of Ar gas, pale yellow powder was obtained. Finally, the product was then calcined at 550 ^oC for 2 h in air.

Synthesis of CN-COF

A typical synthesis procedure was as follows: 4,4',4"-(1,3,5-triazine-2,4,6-triyl) trianiline (0.07 mmol), 1, 3, 5-Triformylphloroglucinol (0.13mmol) and g-C_3N_4 (0.3g) were added in 5 mL DMSO. After stirred for 10 minutes in Ar gas, the mixture was heated at 120 °C for 6 hours, and then maintained at 150 °C for 36 hours. After cooled down to room temperature, the precipitant was collected by filtration and washing with methanol. The obtained powder was dried at 70 °C for 5 hours.

Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a DX2700 X-ray (Dandong, China) diffractometer with Cu Kα radiation at 5° $\min^{-1}$ scanning speed. Transmission electron microscopy images (TEM) were obtained on a Tecnai G2 F20 S-TWIN instrument. Fourier transform infrared (FTIR) spectra were performed on a Perkin-Elmer spectrometer. The diffuse reflectance spectra (DRS) were recorded on a UV–vis spectrophotometer (UV3600, Shimadzu). The photoluminescence (PL) spectra were collected with a photoluminescence spectrophotometer (Hitachi F-7000). The photoluminescence lifetime spectra (TRPS) were obtained on a Fluorolog-3 spectrofluorometer (Horiba JobinYvon) with an excitation wavelength of 279 nm and detection wavelength of 500 nm. The photocurrent response, Mott-schottky plots and electrochemical impedance spectroscopy (EIS) were measured with electrochemical workstation (CHI660E) in a three electrodes model, utilizing a Pt piece as the counter electrode and an Ag/AgCl electrode as the reference electrode. 0.1 mol.L^{-1} sodium sulfate was used as electrolyte solution. The N_2 adsorption experiments were carried on MicroActive for ASAP 2460 Version 2.01. Solid-state Nuclear Magnetic Resonance (SNMR) experiments were performed on Bruker AVANCE Ш 600 spectrometer at a resonance frequency of- 600.1 MHZ and 150.9 MHZ, respectively. TGA were tested by NETZSCHSTA 449F3 STA449F3A-1379-M instrument.

Photocatalytic activity measurements

The photocatalytic water splitting reaction was measured with a typical top-irradiation photocatalytic system. Traditionally, 100 mg photocatalyst was added in 200 mL aqueous triethanolamine sacrificial reagent solution (10 %). Pt was loaded on the surface of catalyst by in situ photo-reduction H_2PtCl_6. A 300 W xenon lamp (Ceralux 300BF) fitted with a cut off filter ($\lambda >$ 420 nm) served as light source. Before photocatalytic reaction, the system was vacuumed. The temperature was maintained at room temperature by circulating water which was regulated by a DLSB Low Temp Pump. The generated gas was analyzed on a gas chromatography (SPSIC, GC-112AT, argon carrier) every 1 h.

Apparent quantum efficiency (AQE) measurements

The apparent quantum efficiency was measured using the same apparatus as the photocatalytic H_2 evolution test. 0.1g CN-COF was suspended in 200 mL 10% triethanolamine solution containing appropriate H_2PtCl_6. The solution was illuminated by 300 W Xe lamp (Ceralux 300BF) equipped with filter at 425 nm. The amount of hydrogen evolution was tested using gas chromatography and the incident photons was measured using a ThorLabs S120C photodiode power sensor. The apparent quantum efficiency were estimated using Equation as follows:

$$\eta = \frac{2 \times \text{moles of } \mathrm{H_2} \text{ evolved}}{\text{moles of the incident photons}} \times 100\%$$

Figures and Tables

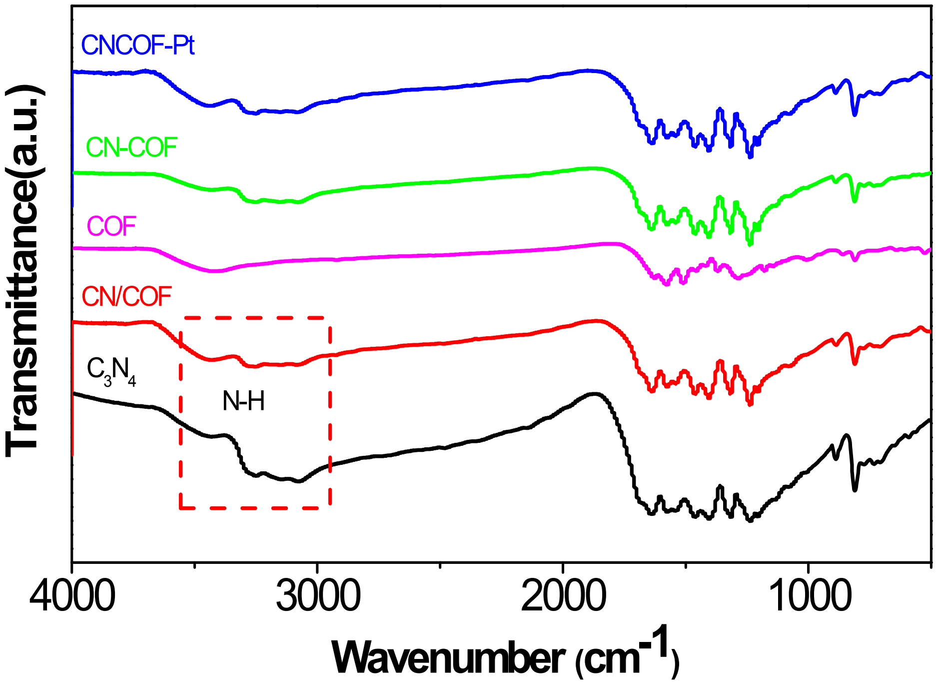


Figure S1. FT-IR spectra of g-C_3N_4, COF, CN/COF, CN-COF and CNCOF-Pt.

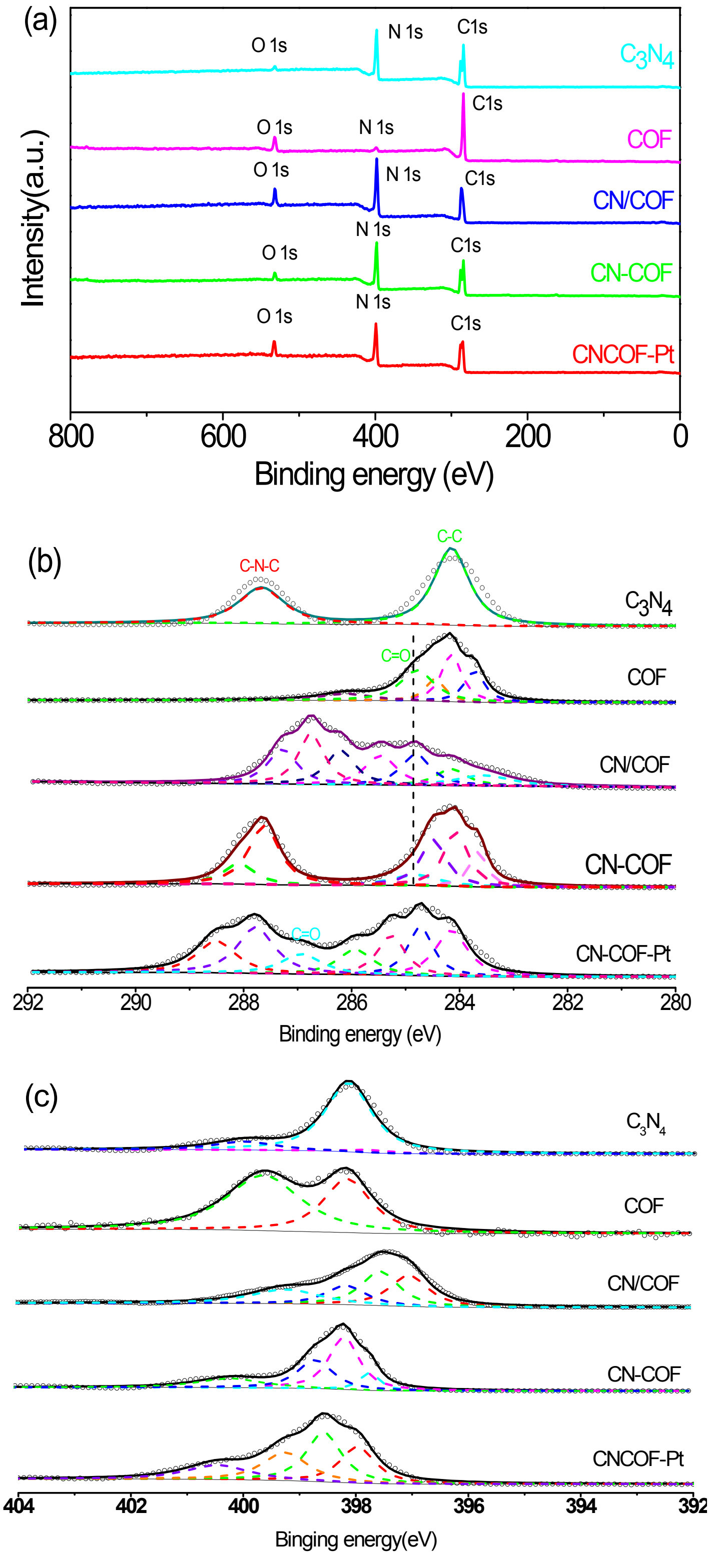


Figure S2. XPS spectra of the samples. (a) The survey scan, (b) High-resolution spectra of C 1s for samples, and (c) High-resolution spectra of C 1s for the samples.

The survey XPS spectrum of samples (Figure S2a) confirms the coexistence of the elements of C, N, and O in the sample. For g-C_3N_4, the high resolution spectrum of C 1s can be fitted into two peaks at 284.15 eV (C-C) and 287.8 eV (C-N-C), and the N 1s spectrum can be divided to three peaks at 397.9 (C-N=C), 398.3 (N-$(C)_3$) and 400.2 eV (C-N-H). For COF, the high resolution spectrum of C 1s can be fitted into four peaks at 284.15, 284.5, 284.8 and 286.1 eV, corresponding to C-C,C=C,C=O and N-C=N bonds, respectively, while the N 1s spectrum can be divided to two peaks at 398.2 and 399.7 eV, corresponding to C-N=C and C-N-H bonds, respectively.

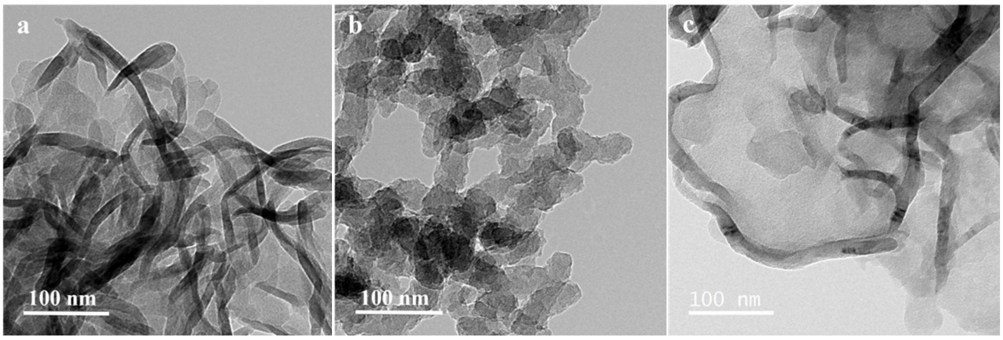


Figure S3. TEM images of g-C_3N_4 (a), COF (b) and CN/COF (c).

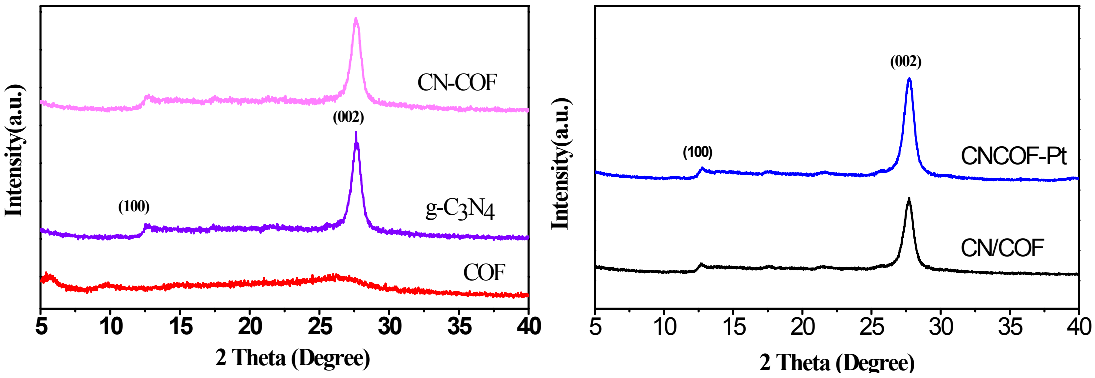


Figure S4. Powder X-ray diffraction pattern of (left) g-C_3N_4, COF, CN-COF, and (right) CN/COF and CNCOF-Pt.

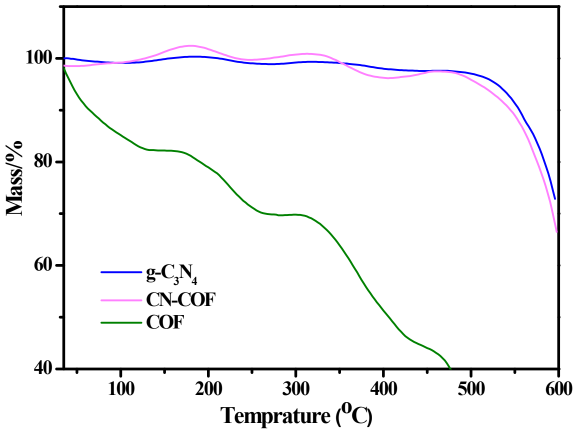


Figure S5. Thermal gravimetric analysis of g-C_3N_4, COF and CN-COF.

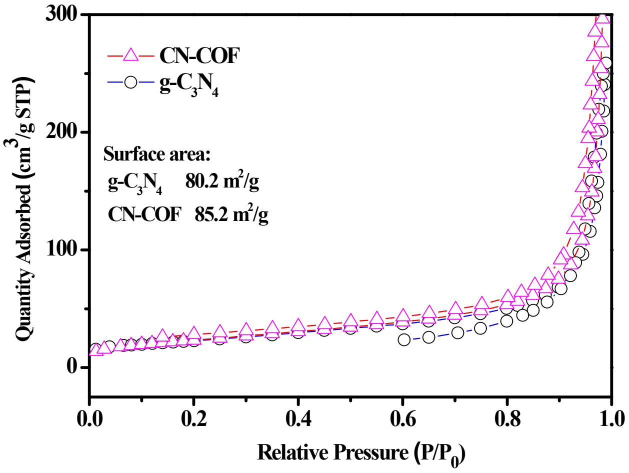
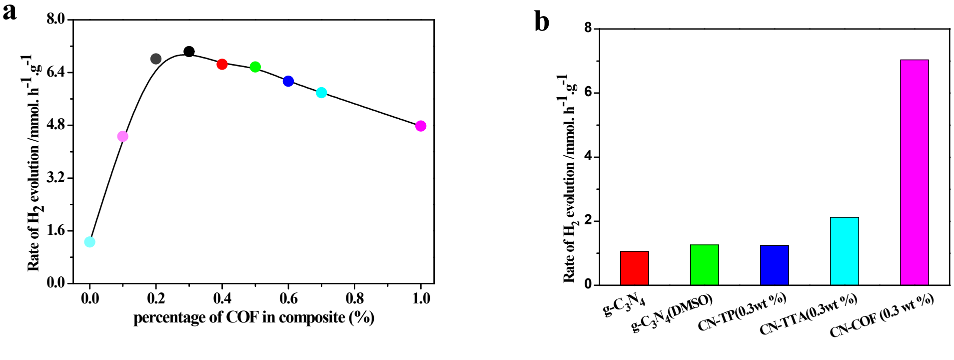


Figure S6. N_2 adsorption-desorption isotherm of g-C_3N_4 and CN-COF.



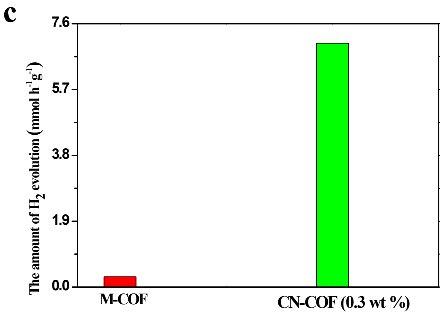


Figure S7. (a) H_2 production rate of CN-COF (x %). (b) H_2 production rate of g-C_3N_4, g-C_3N_4 (DMSO), CN-TP, CN-TTA and CN-COF. (c) H_2 production rate of M-COF, CN-COF.

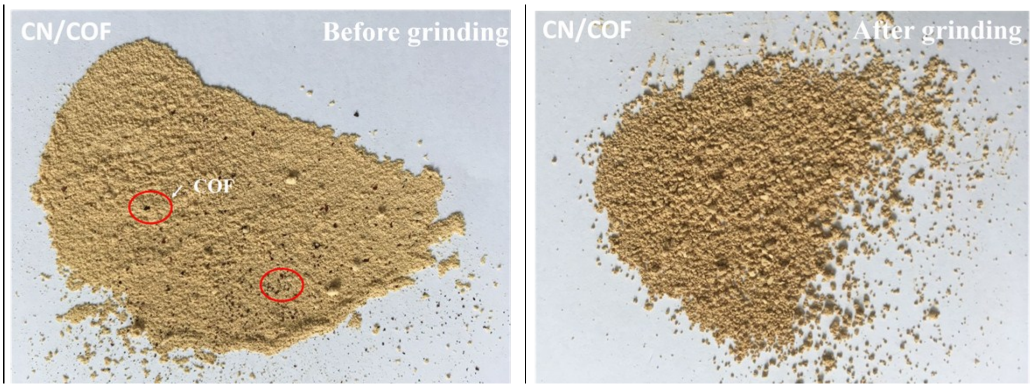


Figure S8. Pictures of CN/COF.

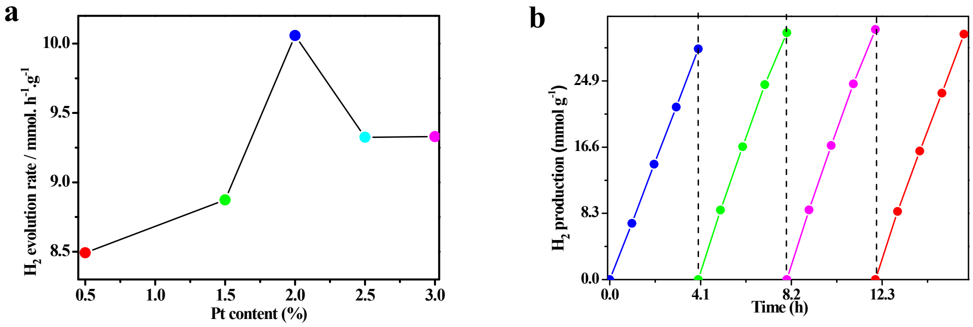


Figure S9. (a) H_2 production rate of CN-COF (3%)-Pt (x%). (b)Photocatalytic stablility test of CN-COF.

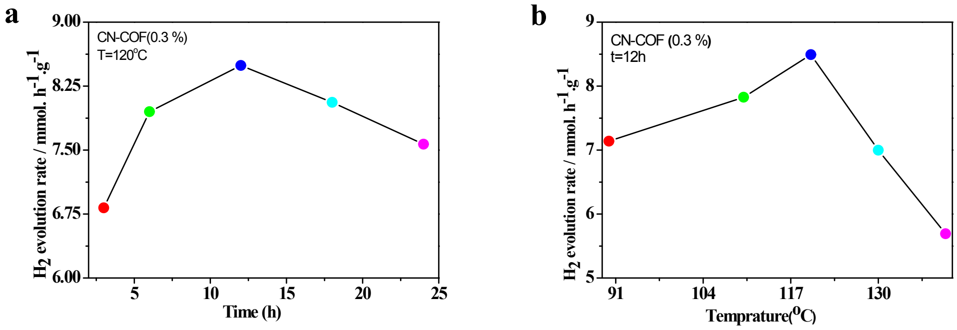


Figure S10. H_2 production rate of CN-COF prepared at different reaction time and temprature.

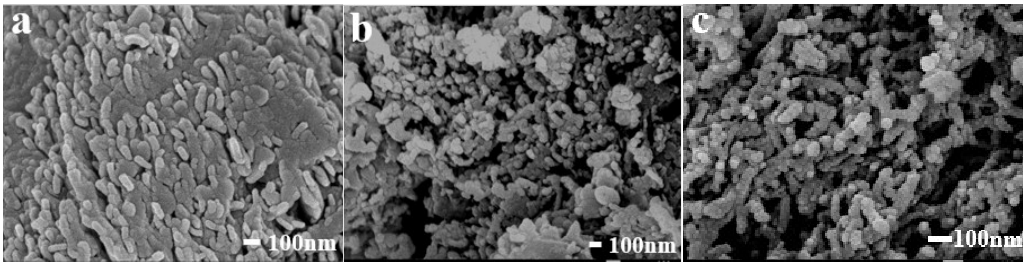


Figure S11. SEM images of g-C_3N_4 (a), CN-COF (b), and COF (c).

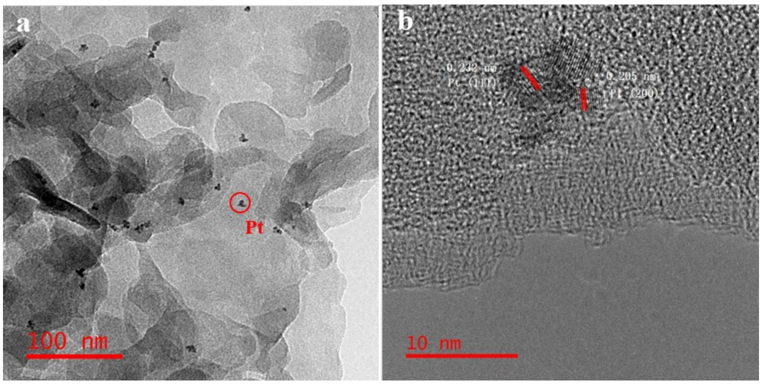


Figure S12. TEM (a) and HRTEM (b) images of CNCOF-Pt.

Table S1 Comparison of photocatalytic H_2 production rate of g-C_3N_4 based photocatalyst.

Photocatalyst	Light source	Reaction Conditions	H_2 generation rate (μmol·g^{-1}·h^{-1})	Apparent quantum yield	Ref.
g-C_3N_4-COF	300 W Xe lamp, λ > 420 nm	2 wt % of Pt as co-catalyst; 10% TEOA solution	10058	20.7% at 425 nm	This work
Bi_2MoO_6/g-C_3N_4	300 W Xe lamp, λ > 420 nm	3 wt% of Pt co-catalyst; 10% TEOA solution	563.4	N/A	[S2]

Pt/g-C_3N_4	300 W Xe lamp, λ > 400 nm	0.16wt % of Pt co-catalyst; 10% TEOA solution	6360	N/A	[S3]
CoS_x/g-C_3N_4	350 W Xe lamp, λ > 400 nm	20% TEOA solution	629	N/A	[S4]
co-doped g-C_3N_4	350 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 25% methanol solution	3820	N/A	[S5]
amorphous carbon/g-C_3N_4	350 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 15% TEOA solution	212.8	0.9% (420 nm)	[S6]
NiS/g-C_3N_4	300 W Xe lamp, λ > 420 nm	15% TEOA solution	482	1.9 %(440 nm)	[S7]
C-TiO_2@g-C_3N_4	300 W Xe lamp, λ > 420 nm	10% methanol solution	35.6	N/A	[S8]
defect-modified g-C_3N_4	300 W Xe lamp, λ > 420 nm	3 wt% of Pt co-catalyst; 10% TEOA solution	4020	N/A	[S9]
ammonium hydroxide modified g-C_3N_4	300 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 10% TEOA solution	707.58	5.18% (420 nm)	[S10]
g-C_3N_4-N-ZnO	300 W Xe lamp, λ > 420 nm	0.3 M Na_2S and 0.3 M Na_2SO_3	18836	N/A	[S11]
α-Fe_2O_3/g-C_3N_4	300 W Xe lamp, λ > 400 nm	3 wt % of Pt co-catalyst; 10% TEOA solution	31400	44.35% (420 nm) 19.80% (435 nm)	[S12]
(C-ring)−C_3N_4	300 W Xe lamp, λ > 420 nm	3 wt% of Pt co-catalyst; without sacrificial electron donor	371	5 % (420 nm)	[S13]
g-C_3N_4/SiC	300 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 10% TEOA solution	182	N/A	[S14]
g-C_3N_4 nanosheets	300 W Xe lamp, λ > 400 nm	3 wt% of Pt co-catalyst; 105 TEOA solution, 0.20mol K_2HPO_4	18940	26.1% (420nm)	[S15]

PTCDIs/Pt/g-C_3N_4	400 W Xe lamp, λ > 420 nm	10% TEOA solution	152	0.31% (420 nm)	[S16]
Cu_2O@g-C_3N_4	300 W Xe lamp, λ > 420 nm	0.5 wt% of Pt co-catalyst; 10% TEOA solution	265	N/A	[S17]
WO_3/g-C_3N_4	300 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 10% TEOA solution	400	N/A	[S18]
ZnCr LDH/g-C_3N_4	300 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 10% TEOA solution	186.97	N/A	[S19]
SnS_2/g-C_3N_4	300 W Xe lamp, λ > 420 nm	3wt% of Pt co-catalyst; 10% TEOA solution	972.6	N/A	[S20]
Fe_2O_3/g-C_3N_4	350 W Xe lamp, λ > 420 nm	1wt% of Pt co-catalyst, 15% TEOA solution	398.9	N/A	[S21]
CQD‑implanted g‑C_3N_4 nanotubes	300 W Xe lamp, λ > 400 nm	3 wt% of Pt co-catalyst; 10% TEOA solution	3538.3	10.94% at 420 nm	[S22]
Mo_2C@C/2D g-C_3N_4	300 W Xe lamp, λ > 400 nm	10% TEOA solution	2269.47	9.07% at 405nm	[S23]
Pd/2D-C_3N_4	300 W Xe lamp, λ > 400 nm	10% TEOA solution	1208.6	3.8% at 420 nm	[S24]
MoS_2/g-C_3N_4	300 W Xe lamp, λ > 400 nm	1wt% of Pt co-catalyst, 25% methanol solution	231	N/A	[S25]
PGCN/TNTs	300 W Xe lamp, λ > 400 nm	3wt% of Pt co-catalyst, 12% methanol Solution	1364	6.32% at 420 nm	[S26]
Cr_2O_3/g-C_3N_4	300 W Xe lamp, λ > 420 nm	1 wt% of Pt co-catalyst; 10% TEOA solution	109	N/A	[S27]

Reference

[1]Zhang, Y.; Mao, F.; Yan, H.; Liu, K.; Cao, H.; Wu, J.; Xiao, D. *J. Mater. Chem. A.* 2015, **3**, 109.

[2] J. Li, Y. C. Yin, E. Z. Liu, Y. N. Ma, J. Wan, J. Fan, X. Y. Hu, *J hazard mater.,*2017,321,183-

192.

[3] X.G. Li, W.T. Bi, L. Zhang, S. Tao, W.S. Chu, Q. Zhang, Y. Luo, C.Z. Wu, Y. Xie, *Adv. Mater.,* 2016, **28**, 2427–2431.

[4] J. W. Fu, C.B. Bie, B. Cheng, C.J. Jiang, J.G. Yu, *ACS Sustainable Chem. Eng.* 2018, **6**, 2767−2779.

[5] S.W. Cao, Q. Huang, B.C. Zhu, J.G. Yu, *J Power Sources*, 2017,**351**, 151-159.

[6] Q.L. Xu, B. Cheng, J.G. Yu, G. Liu, *Carbon* 2017, **118** , 241-249.

[7] J.D. Hong, Y.S. Wang, Y.B. Wang, W. Zhang, R. Xu, *ChemSusChem* .,2013, **6**, 2263 – 2268.

[8] Y.J. Zou, J.W. Shi, D.D. Ma, Z.Y. Fan , L. Lu , C.M. Niu, *Chem. Eng. J.* 2017,**322**, 435–444.

[9] G.G. Liu , G.X. Zhao , W. Zhou , Y.Y. Liu , H. Pang , H.B. Zhang , D. Hao , X.G. Meng , P. Li , T. Kako , J.H. Ye, *Adv. Funct. Mater.* 2016, **26**, 6822–6829.

[10] B. Luo, R. Song, D.W. Jing, *Chem. Eng. J.* 2018, **332**, 499-507.

[11] S. Kumar, N. L. Reddy, A. Kumar, M. V. Shankar, V. Krishnan, *Inter. J. Hydrogen energy.*, 2018,**43**,3988-4002.

[12]X.J. She, J.J. Wu, H. Xu,J. Zhong, Y. Wang, Y.H. Song, K.Q. Nie,Y. Liu, Y.C. Yang, M.T.F. Rodrigues, R. Vajtai, J. Lou, D.L. Du, H.M. Li, P.M. Ajayan, *Adv. Energy Mater.,* 2017, **7**, 1700025. DOI: 10.1002/aenm.201700025

[13] W. Che , W.R. Cheng, T. Yao, F.M. Tang, W. Liu, H. Su, Y. Y. Hang, Q.H. Liu, J.K. Liu, F.C. Hu, Z.Y. Pan, Z.H. Sun, S.Q. Wei, *J. Am. Chem. Soc.* 2017, **139**, 3021−3026.
DOI: 10.1021/jacs.6b11878

[14] B. Wang, J.T. Zhang, F. Huang, *Appl. Surf. Sci.,* 2017,**391**, 449–456.

[15] G.G. Liu, T. Wang, H.B. Zhang, X.G. Meng, D. Hao, K. Chang, P. Li, T. Kako, J.H. Ye, *Angew. Chem. Int. Ed.* 2015, **54**, 13561 –13565.
DOI: 10.1002/anie.201505802

[16] S. Chen, C. Wang, B. R. Bunes, Y.X. Li, C.Y. Wang, Li. Zang, *Applied Catalysis A: General* 2015 ,**498**, 63–68.

[17] Li. Liu, Y.H. Qi, J.S.Hu, Y.H. Liang, W.Q. Cui, *Appl. Surf.Sci.* 2015,**351**, 1146–1154.

[18] C. Cheng, J.W. Shi, Y.C. Hu , L.J. Guo, *Nanotechnology* 2017,**28**, 164002.

[19] B. Luo, R. Song, D.W. Jing, *Inter. J. Hydrogen energy.*,2017,**42**,23427-23426.

[20] E.Z. Liu, J.B. Chen, Y.N. Ma, J. Feng, J. Jia , J. Fan, X.Y. Hu, *J Colloid Interf. Sci.,*2018,524,313-324.

[21] Q.L. Xu, B.C. Zhu, C.J. Jiang, B. Cheng, J.G. Yu, *Sol. RRL,* 2018,**2**,1800006.

[22] Y. Wang, X.Q. Liu, J. Liu, B. Han, X.Q. Hu, F.Yang, Z.W. Xu, Y.C. Li, S.R. Jia, Z. Li, Y.L. Zhao, *Angew. Chem. Int. Ed.* 2018, **57**, 5765 –5771.

[23] Y.H. Song, K.X. Xia, Y.M. Gong, H.X. Chen, L. Li, J.J. Yi, X.J. She, Z.G. Chen, J.J. Wu, H.M. Li, H. Xu, *Dalton Trans.,* 2018, **47**, 14706.

[24] Z. Mo, H. Xu, X.J. She, Y.H. Song, P.C. Yan , J.J. Yi, X.W. Zhu , Y.C. Lei, S.Q. Yuan, H.M. Li, *Appl. Surface Sci.*, 2019,**468**, 151–157.

[25] Y.M. Tian, L. Ge, K.Y. Wang, Y.S. Chai, *Mater. Charact.,* 2014, **87**, 70-73.

[26] Y. Wang, X.Q. Liu, C.C. Zheng, Y.C. Li, S.R. Jia, Z. Li, Y.L. Zhao, *Adv. Sci.* 2018, **5**, 1700844.

[27] J.W. Shi, C. Cheng, Y.C. Hu, M.C. Liu, L.J. Guo, *Inter. J. Hydrogen energy.*,2017,**42**,4651-4659.

[28] C.C. Han, Y.Q. Gao, S. Liu , L. Ge, N. Xiao, D.S. Dai, B.R. Xu, C.F. Chen, *Inter. J.*

Hydrogen energy.,2017,**42**,22765-22775.

[29] L.Q. Kong, Y.J. Ji, Z.Z. Dang, J.Q. Yan, P.Li, Y.Y. Li, S.Z. Liu, *Adv. Funct. Mater.* 2018, ***28***, 1800668.

[30] A. Kumar, A. Rana, G. Sharma, M. Naushad, A. H. Al-Muhtaseb, C.S. Guo, A. Iglesias-Juez, F. J. Stadler, *ACS Appl. Mater. Interfaces* 2018, **10**, 40474−40490.