## **Supporting Information**

## An Insight into the Crucial Factors for Photochemical Deposition of Cobalt Cocatalyst on g-C<sub>3</sub>N<sub>4</sub> Photocatalyst

Na Zhao, Linggang Kong, Yuming Dong\*, Guangli Wang, Xiuming Wu and Pingping Jiang

\* E-mail: dongym@jiangnan.edu.cn

Fax: +86 510 85917763

International Joint Research Center for Photoresponsive Molecules and Materials,

School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122,

People's Republic of China.



**Figure S 1**. Photocatalytic HER activity of Co-T/g-C<sub>3</sub>N<sub>4</sub> (T=0, 20, 30, 40, 50, 60 and 120 min), and the data were obtained by photocatalytic processes of 5 mg photocatalyst in 15 mL 20 vol% TEOA aqueous solution for 2 h.



**Figure S 2**. IR spectra of pure  $g-C_3N_4$  and  $Co-T/g-C_3N_4$  (T=20, 50, 120) with different deposition time.



Figure S 3. Raman spectra of Co-T/g-C<sub>3</sub>N<sub>4</sub> (T=0, 50, and 120 min) excited by laser of 785 nm.



Figure S 4. UV-vis diffuse reflectance spectra of Co-T/g-C<sub>3</sub>N<sub>4</sub> (T=0, 50 and 120 min).



Figure S 5. XRD of Co-50/g-C $_3N_4$  before and after irradiation for 48 h.



Figure S 6. IR of Co-50/g-C<sub>3</sub>N<sub>4</sub> before and after irradiation for 48 h.



Figure S 7. TEM image of  $Co/g-C_3N_4$  after irradiation for 48 h.



Figure S 8. EDX-Mapping image of  $Co/g-C_3N_4$  after irradiation for 48 h.



Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths		Enter Start and End Wavelengths			
Start Wavelength	365.000	Area Balance Factor	Start Wavelength	385.000	
End Wavelength	385.000	1	End Wavelength	700.000	
A	rea	Err	Are	a	Err
La	308116.33	555.08227	Ea	30097.29	283.01464
Lc	1.61E+06	1269.70679	Ec :	55382.48	235.33483



	Ente	er Start and End Wavelen	gths	Ent	er Start and End Wavelen	gths
	Start Wavelength	365.000	Area Balance Factor	Start Wavelength	385.000	
	End Wavelength	385.000	1	End Wavelength	700.000	
Area		Err	Area		Err	
La 240185.53		490.08727	<i>Ea</i> 33939.51		184.2268	
<i>Lc</i> 1.61E+06		1269.68321	<i>Ec</i> 49860.96		223.29567	

Figure S 9. The emission quantum yields of (a)  $g-C_3N_4$  and (b)  $Co-50/g-C_3N_4$  compared with blank samples.

Catalysts	Mass fraction	Sacrificial agent	Light source	Activity $(\mu mol g^{-1} h^{-1})$	Quantum yield	Ref.
Co/ g-C <sub>3</sub> N <sub>4</sub>	2.63 wt%	triethanolamine	300 W Xe lamp	2295	6.2% (400 nm)	This work
Co/CN	0.46 wt%	triethanolamine	300 W Xe lamp	560	/	<b>S</b> 1
Co(OH) <sub>2</sub> / g-C <sub>3</sub> N <sub>4</sub>	30.0 wt%	triethanolamine	300 W Xe lamp	7200	27.3% (550 nm)	S2
CoP/ g-C <sub>3</sub> N <sub>4</sub>	0.25 wt%	triethanolamine	300 W Xe lamp	474.4	/	S3
CoS/ mpg-CN	1.0 at %	triethanolamine	300 W Xe lamp	740	/	S4
CoIII(dm gH) <sub>2</sub> pyCl /g-C <sub>3</sub> N <sub>4</sub>	/	triethanolamine	300 W Xe lamp	216.7	0.62% (365 nm)	S5
Co(OH) <sub>2</sub> / CdS	6.8 mol %	ethanol	500 W Xe lamp	61	/	S6
Co <sub>2</sub> P/ CdS	31.25 wt%	DL-mandelic acid	LED light 30 * 3 W	19373	6.8% (≥420 nm)	S7
Co/CdS			350 W Xe lamp	796	/	S8
Co(OH) <sub>2</sub> / CdS	1000000000000000000000000000000000000	lactic acid		1958	/	
Co <sub>3</sub> O <sub>4</sub> / CdS				3014	9.7% (420 nm)	
CoS <sub>x</sub> / TiO <sub>2</sub>	5 mol%	ethanol	300 W Xe lamp	838	/	S9
Co/TiO <sub>2</sub>	0.1 wt%	methanol	250 W high pressure mercury lamp	200	/	S10
Co/TiO <sub>2</sub>	1.0 wt%	glycerol	solar light	11021	/	S11
Co/TiO <sub>2</sub>	0.3 wt%	triethanolamine	150 W halogen lamp	1160	/	S12

Table S 1. Photocatalytic  $H_2$  evolution over different semiconductors modified with

cobalt-based cocatalysts.

## References

S1 Chen, P. W.; Li, K.; Yu, Y. X.; Zhang, W. D. Cobalt-Doped Graphitic Carbon Nitride Photocatalysts with High Activity for Hydrogen Evolution. *Appl. Surf. Sci.*2017, 392, 608-615.

S2 Li, Z.; Wu, Y. Q.; Lu, G. X. Highly Efficient Hydrogen Evolution over  $Co(OH)_2$ <sub>N</sub>anoparticles Modified g-C<sub>3</sub>N<sub>4</sub> Co-Sensitized by Eosin Y and Rose Bengal under Visible Light Irradiation. *Appl. Catal. B.* **2016**, 188, 56-64.

S3 Yi, S. S.; Yan, J. M.; Wulan, B. R.; Li, S. J.; Liu, K. H.; Jiang, Q.
Noble-Metal-Free Cobalt Phosphide Modified Carbon Nitride: An Efficient
Photocatalyst for Hydrogen Generation. *Appl. Catal. B.* 2017, 200, 477-483.

S4 Zhu, Y. S.; Xu, Y.; Hou, Y. D.; Ding, Z. X.; Wang, X. C. Cobalt Sulfide Modified Graphitic Carbon Nitride Semiconductor for Solar Hydrogen Production. *Int. J. of Hydrogen Energy.* **2014**, 39, 11873-11879.

S5 Cao, S. W.; Liu, X. F.; Yuan, Y. P.; Zhang, Z. Y.; Fang, J.; Loo, S. C.; Barber, J.; Sum, T. C.; Xue, C. Artificial Photosynthetic Hydrogen Evolution over g-C<sub>3</sub>N<sub>4</sub> Nanosheets Coupled with Cobaloxime. *Phys. Chem. Chem. Phys.* **2013**, 15, 18363-18366.

S6 Zhang, L. J.; Zheng, R.; Li, S.; Liu, B. K.; Wang, D. J.; Wang, L. L.; Xie, T. F.
Amorphous Co<sub>3</sub>O<sub>4</sub> Modified CdS Nanorods with Enhanced Visible-Light
Photocatalytic H<sub>2</sub>-Production Activity. *Appl. Mater. Interfaces.* 2014, 6, 13406-13412.
S7 Cao, S.; Chen, Y.; Hou, C. C.; Lv, X. J.; Fu, W. F. Cobalt Phosphide as a Highly
Active Non-Precious Metal Cocatalyst for Photocatalytic Hydrogen Production under
Visible Light Irradiation. *J. Mater. Chem. A.* 2015, 3, 6096-6101.

S8 Lang, D.; Cheng, F. Y.; Xiang, Q. J. Enhancement of Photocatalytic H<sub>2</sub>
Production Activity of CdS Nanorods by Cobalt-Based Cocatalyst Modification. *Catal. Sci. Technol.* 2016, 6, 6207-6216.

S9 Yu, Z. M.; Meng, J. L.; Xiao, J. R.; Li, Y.; Li, Y. D. Cobalt Sulfide Quantum Dots Modified TiO<sub>2</sub> Nanoparticles for Efficient Photocatalytic Hydrogen Evolution. *Int. J. of Hydrogen Energy.* **2014**, 39, 15387-15393. S10 Lin, J. D.; Yan, S.; Huang, Q. D.; Fan, M. T.; Yuan, Y. Z.; Tan, T. Y.; Liao, D.
W. TiO<sub>2</sub> Promoted by Two Different Non-Noble Metal Cocatalysts for Enhanced Photocatalytic H<sub>2</sub> Evolution. *Appl. Surf. Sci.* 2014, 309, 188-193.

Sadanandam, G.; Lalitha, K.; Kumari, V. D.; Shankar, M. V.; Subrahmanyam,
M. Cobalt Doped TiO<sub>2</sub>: A Stable and Efficient Photocatalyst for Continuous
Hydrogen Production from Glycerol: Water Mixtures under Solar Light Irradiation. *Int. J. of Hydrogen Energy.* 2013, 38, 9655-9664.

S12 Tran, P. D.; Xi, L.F.; Batabyal, S. K.; Wong, L. H.; Barber, J.; Loo, J. S. C. Enhancing the Photocatalytic Efficiency of TiO<sub>2</sub> Nanopowders for H<sub>2</sub> Production by Using Non-Noble Transition Metal Co-Catalysts. *Phys. Chem. Chem. Phys.* **2012**, 14, 11596-11599.