

## Supporting Information

### **Hierarchical Z-Scheme g-C<sub>3</sub>N<sub>4</sub>/Au/ZnIn<sub>2</sub>S<sub>4</sub> Photocatalyst for Highly Enhanced Visible-Light Photocatalytic Nitric Oxide Removal and Carbon Dioxide Conversion**

Guping Zhang,<sup>a</sup> Xingwang Zhu,<sup>b</sup> Dongyun Chen,<sup>\*,a</sup> Najun Li,<sup>a</sup> Qingfeng Xu,<sup>a</sup> Hua Li,<sup>a</sup> Jinghui He,<sup>a</sup> Hui Xu,<sup>b</sup> and Jianmei Lu<sup>\*,a</sup>

<sup>a</sup>College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology Soochow University, Suzhou 215123 (P.R. China)

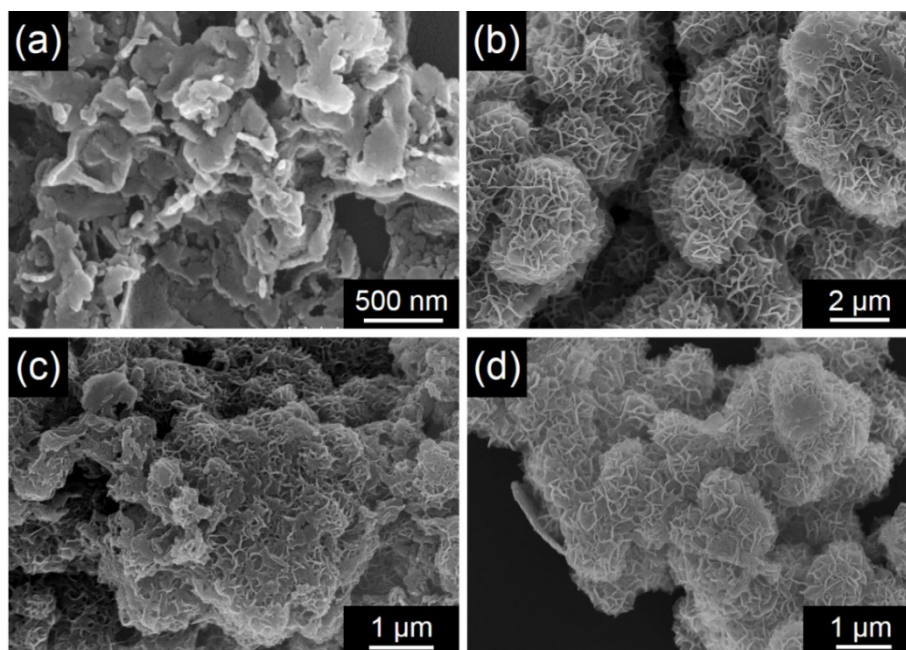
<sup>b</sup>Institute for Energy Research, Jiangsu University, Zhenjiang 212013 (P.R. China)

E-mail: dychen@suda.edu.cn; lujm@suda.edu.cn

## **Table of Contents**

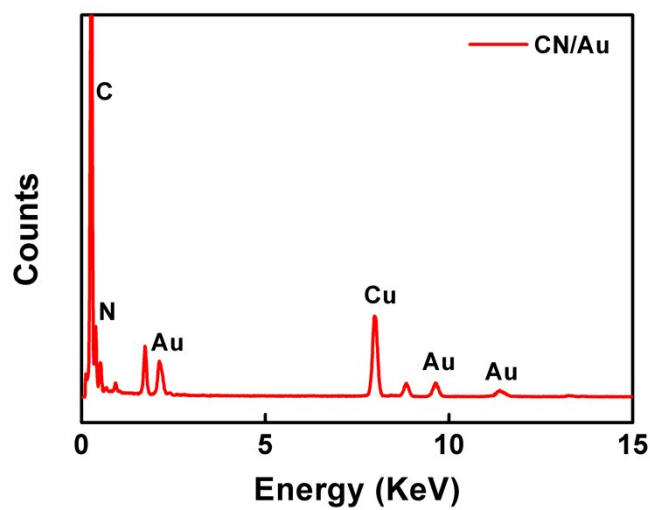
- S1. SEM images of as-prepared samples**
- S2. TEM-EDX of as-prepared samples**
- S3. Survey XPS spectrum of CN/Au/ZIS-1 sample**
- S4. Valence-band XPS of CN and ZnIn<sub>2</sub>S<sub>4</sub> samples**
- S5. Pore size distribution curve of CN/Au/ZIS-1 sample**
- S6. EIS and time-resolved transient PL spectra of as-prepared samples**
- S7. Photocatalytic activities of prepared samples and Detecting of NO<sub>2</sub>**
- S8. Detecting of H<sub>2</sub>O<sub>2</sub> and ·OH**
- S9. Photocatalytic CO<sub>2</sub> conversion without 2,2-bipyridine (bpy)**
- S10. The calculation about the N-balance**
- S11. Data comparison of photocatalytic NO removal over different catalysts**
- S12. Data comparison of photocatalytic CO<sub>2</sub> reduction over different catalysts**
- S13. Reference**

## S1. SEM images of as-prepared samples

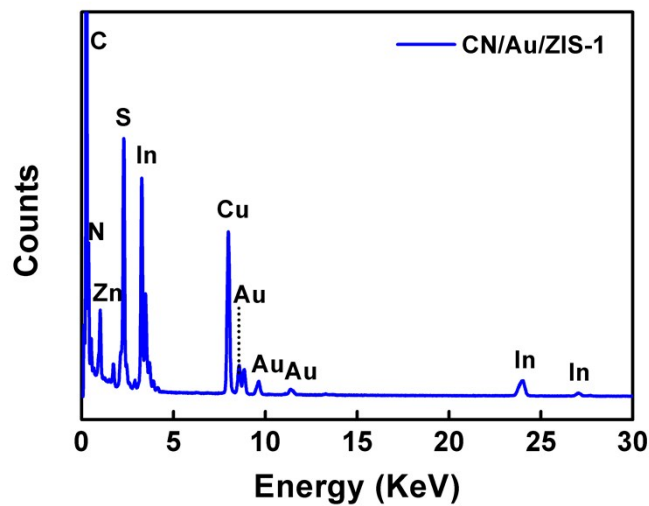


**Figure S1.** SEM images of as-prepared (a) CN, (b) ZnIn<sub>2</sub>S<sub>4</sub>, (c) CN/Au/ZIS-0.5 and (d) CN/Au/ZIS-2.

## S2. TEM-EDX of as-prepared samples

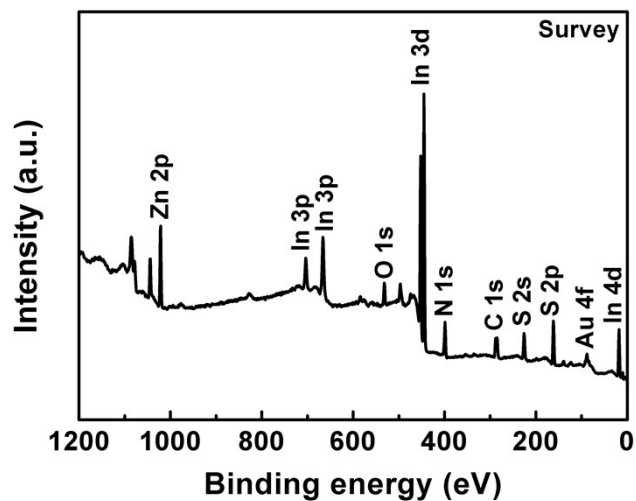


**Figure S2.** TEM-EDX of as-prepared CN/Au.



**Figure S3.** TEM-EDX of as-prepared CN/Au/ZIS-1.

**S3. Survey XPS spectrum of CN/Au/ZIS-1 sample**



**Figure S4.** Survey XPS spectrum of the CN/Au/ZIS-1 sample.

#### S4. Valence-band XPS of CN and ZnIn<sub>2</sub>S<sub>4</sub> samples

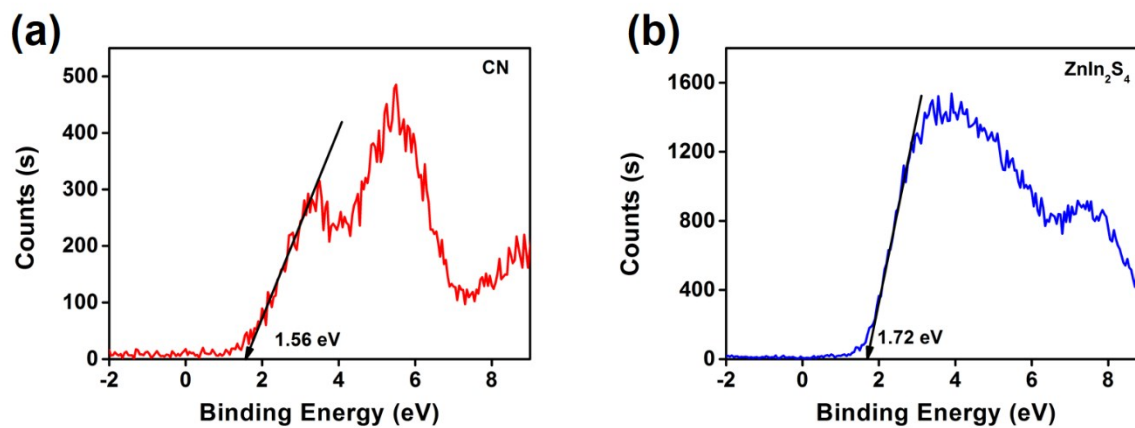


Figure S5. Valence-band XPS spectra of CN and ZnIn<sub>2</sub>S<sub>4</sub> samples.

#### S5. Pore size distribution curve of CN/Au/ZIS-1 sample

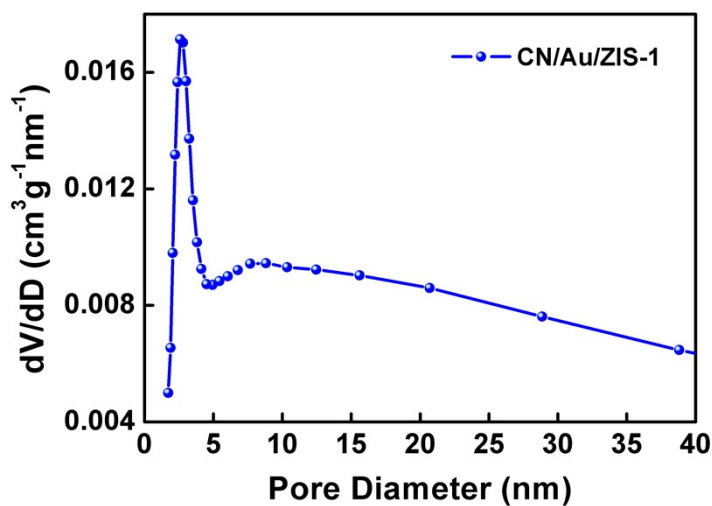


Figure S6. Pore size distribution curves of obtained CN/Au/ZIS-1 sample.

## S6. EIS and time-resolved transient PL spectra of as-prepared samples

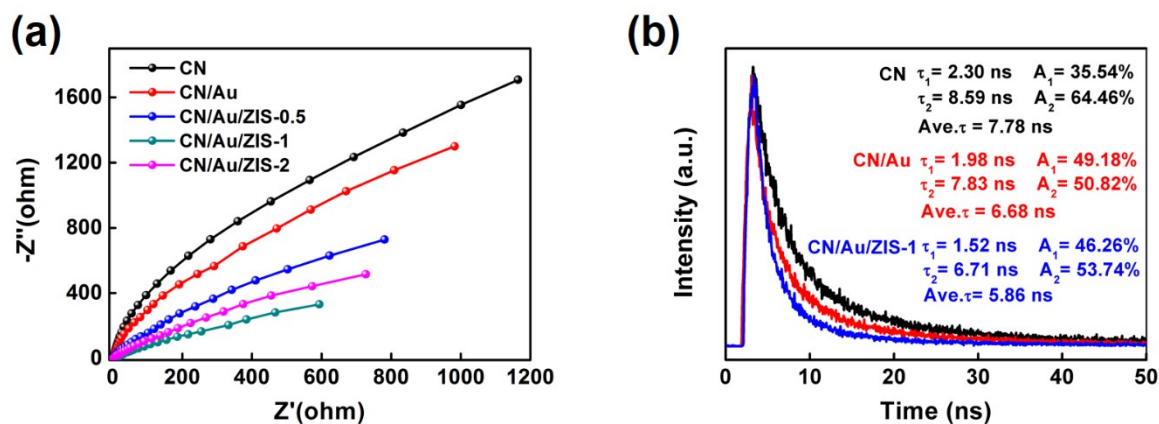


Figure S7. EIS spectra (a) and time-resolved transient PL decay (b) of the as-prepared samples.

## S7. Photocatalytic activities of prepared samples and Detecting of $\text{NO}_2$

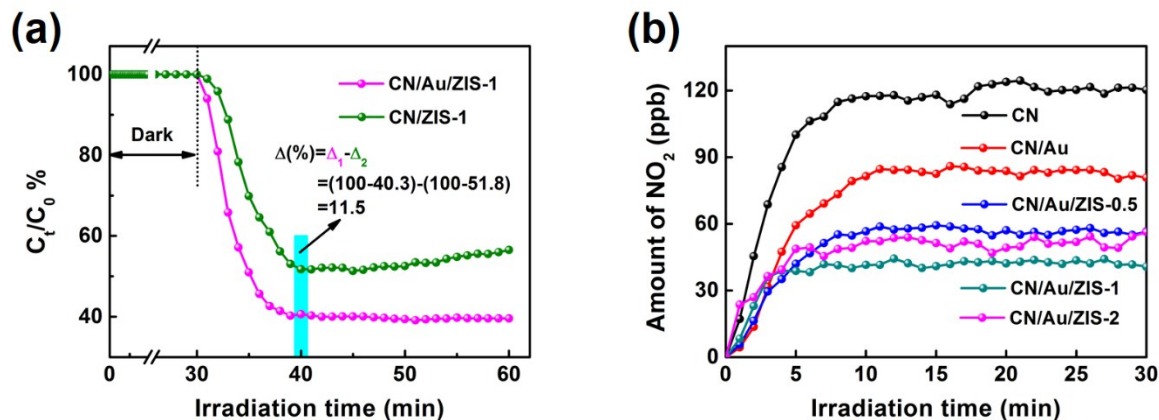
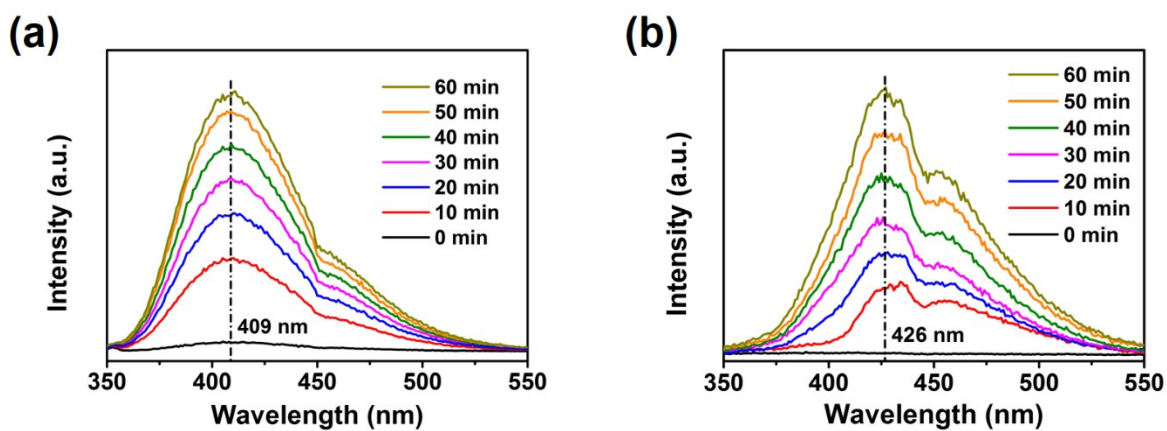


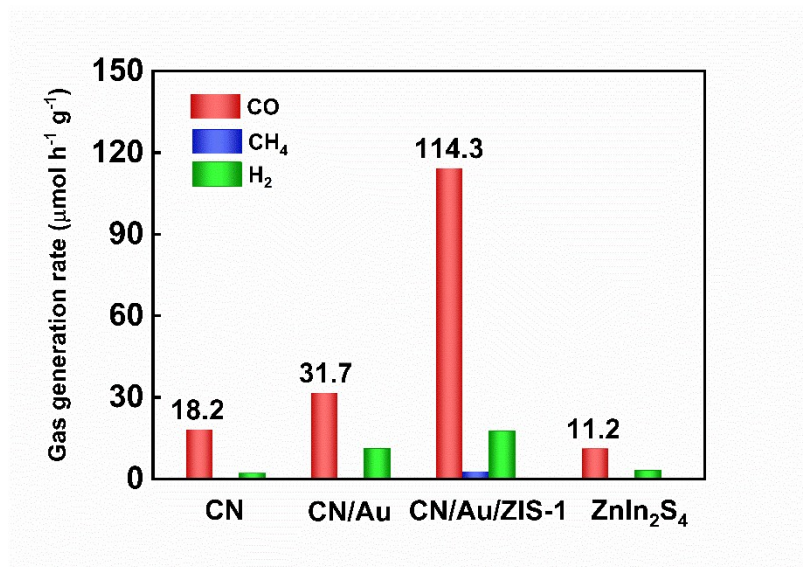
Figure S8. (a) Visible-light photocatalytic activities of the CN/Au/ZIS-1 and CN/ZIS-1 samples for NO removal in air (600 ppb). (b) Monitoring of  $\text{NO}_2$  intermediates during irradiation.

## S8. Detecting of H<sub>2</sub>O<sub>2</sub> and ·OH



**Figure S9.** The fluorescence intensity of (a) H<sub>2</sub>O<sub>2</sub> and (b) ·OH-trapping PL spectra of the CN/Au/ZIS-1 at different visible light irradiation times.

## S9. Photocatalytic CO<sub>2</sub> conversion without 2,2-bipyridine (bpy)



**Figure S10.** CO<sub>2</sub> photoreduction activities of different samples without 2,2-bipyridine (bpy).

### S10. The calculation about the N-balance

The concentration of  $\text{NO}_3^-$  detected by ion chromatography, the washing solution (1000 mL) was concentrated 100 times before the detection. Therefore, the concentration of  $\text{NO}_3^-$  in washing solution should be 0.016 mg/L.

$$(1) \text{ The consumption of NO } (C_{\text{NO}}): C_{\text{NO}} = \sum_{t=1}^{t=30} \text{NO}c = 8746 \text{ ppb} = 8.746 \text{ ppm.}$$

$$\text{The concentration of consumption NO } (C_{\text{NO}}) \text{ is: } C_{\text{NO}} = \frac{30 \times 8.746}{22.4} = 11.713 \text{ } \mu\text{g/L};$$

$$(2) \text{ The generated NO}_2 \text{ } (C_{\text{NO}_2}) \text{ is: } C_{\text{NO}_2} = \sum_{t=1}^{t=30} \text{NO}_2c = 3153 \text{ ppb} = 3.153 \text{ ppm.}$$

$$\text{The concentration of NO which converted to NO}_2 \text{ } (C_{\text{NO/NO}_2}) \text{ is: } C_{\text{NO/NO}_2} = \frac{30 \times 3.153}{22.4} = 4.223 \text{ } \mu\text{g/L};$$

(3) The concentration NO which converted to  $\text{HNO}_3$  ( $C_{\text{NO/HNO}_3}$ ) is:

$$C_{\text{NO/NO}_3^-} = \frac{0.016}{62} \times 30 = 0.007742 \text{ mg/L} = 7.742 \text{ } \mu\text{g/L};$$

(4)  $C_{\text{NO/NO}_3^-} + C_{\text{NO/NO}_2} = 7.742 + 4.223 = 11.965 \mu\text{g/L}$ ; this value approximately equal to that of consumption NO, therefore, the formed  $\text{NO}_2$ , and  $\text{NO}_3^-$  can meet with the consumed NO.



**S11. Table S1** Data comparison of photocatalytic NO removal over different catalysts.

<b>Catalyst</b>	<b>Catalyst (mg)</b>	<b>NO (ppb)</b>	<b>Light type (Xe lamp)</b>	<b>Time (min)</b>	<b><math>\eta_{(\text{NO})}</math> (%)</b>	<b>Ref</b>
Bi <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	200	400	300 W	60	37.0	[1]
CQDs-FeOOH	100	400	300 W	30	34.0	[2]
BiOBr-graphene	100	400	300 W	30	40.0	[3]
Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> -g-C <sub>3</sub> N <sub>4</sub>	100	400	300 W	30	34.8	[4]
Bi@BiOSi	200	450	150 W	30	50.2	[5]
CN-OLa	100	500	150 W	30	50.4	[6]
LaFeO <sub>3</sub> -SrTiO <sub>3</sub>	100	400	300 W	30	40.0	[7]
g-C <sub>3</sub> N <sub>4</sub> /LaCO <sub>3</sub> OH	100	400	300 W	30	30.3	[8]
SrFe <sub>x</sub> Ti <sub>1-x</sub> O <sub>3-<math>\delta</math></sub>	100	400	300 W	30	35.0	[9]
OV-Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	200	600	150 W	30	50.2	[10]
BiOCl/PPy	100	600	300 W	30	28.0	[11]
BiOBr-3C	200	600	150 W	30	38.7	[12]
PI-g-C <sub>3</sub> N <sub>4</sub>	50	600	300 W	50	47.0	[13]
Au@CN	200	500	150 W	30	41.0	[14]
N-TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	200	600	300 W	30	46.1	[15]

N-doped TiO <sub>2</sub>	100	600	150 W	30	36.5	[16]
<b>g-C<sub>3</sub>N<sub>4</sub>/Au/ZnIn<sub>2</sub>S<sub>4</sub></b>	<b>100</b>	<b>600</b>	<b>300 W</b>	<b>30</b>	<b>59.7</b>	<b>This work</b>

**S12. Table S2** Data comparison of photocatalytic CO<sub>2</sub> reduction over different catalysts.

<b>Catalyst</b>	<b>Experimental system</b>	<b>Light type (Xe lamp)</b>	<b>Products (<math>\mu\text{mol h}^{-1} \text{g}^{-1}</math>)</b>	<b>Ref</b>
In <sub>2</sub> S <sub>3</sub> -CuInS <sub>2</sub>	CoCl <sub>2</sub> , 2,2-bipyridine, TEOA, MeCN	300 W	CO: 19	[17]
g-C <sub>3</sub> N <sub>4</sub>	CoCl <sub>2</sub> , 2,2-bipyridine, TEOA, MeCN	300 W	CO: 6	[18]
BCN	CoCl <sub>2</sub> , 2,2-bipyridine, TEOA, MeCN	300 W	CO: 94	[19]
Nitrogen-rich g-C <sub>3</sub> N <sub>4</sub> nanotubes	CoCl <sub>2</sub> , 2,2-bipyridine, TEOA, MeCN	300 W	CO: 103.6	[20]
UiO-66/CNNS	TEOA, MeCN	300W	CO: 9.79	[21]
N-Ta <sub>2</sub> O <sub>5</sub>	[Ru(dcbpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup> TEOA	300 W	HCOOH: 70	[22]
<b>RuRu'/NS-C<sub>3</sub>N<sub>4</sub></b>	Ag, EDTA·2Na	300 W	HCOO <sup>-</sup> : 57.5	[23]
Helical g-C <sub>3</sub> N <sub>4</sub>	CoCl <sub>2</sub> , TEOA and MeCN	300 W	CO: 89	[24]
CeO <sub>2</sub> homojunction	0.5 wt %Pt/0.5 wt % MnO <sub>x</sub> , CO <sub>2</sub> and H <sub>2</sub> O	300 W	CH <sub>4</sub> : 0.086	[25]
GaN nanowires array	0.5 wt %Pt, CO <sub>2</sub> and H <sub>2</sub> O vapor	300 W	CH <sub>4</sub> : 14.8	[26]

$\text{Cu}_3(\text{BTC})_2@\text{TiO}_2$	$\text{CO}_2$ and $\text{H}_2\text{O}$ vapor	300 W	$\text{CH}_4$ : 2.6	[27]
$\text{CaTaO}_2\text{N}$	1.0 wt % Ag, $\text{CH}_3\text{OH}$ , $\text{CO}_2$ bubbled	500 W	$\text{CO}$ : 0.35	[28]
<b><math>\text{g-C}_3\text{N}_4/\text{Au}/\text{ZnIn}_2\text{S}_4</math></b>	<b><math>\text{CoCl}_2</math>, 2,2-bipyridine, TEOA, MeCN</b>	<b>300 W</b>	<b><math>\text{CO}</math>: 242.3</b>	<b>This work</b>

---

### S13. Reference

- [1] Y. Lu, Y. Huang, J. Cao, W. Ho, Q. Zhang, D. Zhu, S. Lee, Insight into the Photocatalytic Removal of NO in Air over Nanocrystalline  $\text{Bi}_2\text{Sn}_2\text{O}_7$  under Simulated Solar Light, *Ind. Eng. Chem. Res.* 2016, **55**, 10609-10617.
- [2] Y. Huang, Y. Gao, Q. Zhang, Y. Zhang, J. Cao, W. Ho, S. Lee, Biocompatible FeOOH-Carbon quantum dots nanocomposites for gaseous  $\text{NO}_x$  removal under visible light: Improved charge separation and High selectivity, *J. Hazard. Mater.* 2018, **354**, 54-62.
- [3] Z. Ai, W. Ho, S. Lee, Efficient visible light photocatalytic removal of NO with BiOBr-graphene nanocomposites, *J. Phys. Chem. C* 2011, **115**, 25330-25337.
- [4] Z. Wang, Y. Huang, W. Ho, J. Cao, Z. Shen, S. Lee, Fabrication of  $\text{Bi}_2\text{O}_2\text{CO}_3/\text{g-C}_3\text{N}_4$  heterojunctions for efficiently photocatalytic NO in air removal: In-situ self-sacrificial synthesis, characterizations and mechanistic study, *Appl. Catal., B* 2016, **199**, 123-133.
- [5] X. Li, W. Zhang, J. Li, G. Jiang, Y. Zhou, S. Lee, F. Dong, Transformation pathway and toxic intermediates inhibition of photocatalytic NO removal on designed Bi metal@defective  $\text{Bi}_2\text{O}_2\text{SiO}_3$ , *Appl. Catal., B* 2019, **241**, 187-195.
- [6] P. Chen, H. Wang, H. Liu, Z. Ni, J. Li, Y. Zhou, F. Dong, Directional electron delivery and enhanced reactants activation enable efficient photocatalytic air purification on amorphous carbon nitride co-functionalized with O/La, *Appl. Catal., B* 2019, **242**, 19-30.

- [7] Q. Zhang, Y. Huang, S. Peng, Y. Zhang, Z. Shen, J. Cao, W. Ho, S. Lee, D. Pui, Perovskite LaFeO<sub>3</sub>-SrTiO<sub>3</sub> composite for synergistically enhanced NO removal under visible light excitation, *Appl. Catal., B* 2017, **204**, 346-357.
- [8] Z. Wang, H. Yu, C. Long, M. Chen, J. Cao, W. Ho, S. Lee, In situ g-C<sub>3</sub>N<sub>4</sub> self-sacrificial synthesis of a g-C<sub>3</sub>N<sub>4</sub>/LaCO<sub>3</sub>OH heterostructure with strong interfacial charge transfer and separation for photocatalytic NO removal, *J. Mater. Chem. A* 2018, **6**, 972-981.
- [9] Q. Zhang, Y. Huang, S. Peng, T. Huang, J. Cao, W. Ho, S. Lee, Synthesis of SrFe<sub>x</sub>Ti<sub>1-x</sub>O<sub>3-δ</sub> nanocubes with tunable oxygen vacancies for selective and efficient photocatalytic NO oxidation, *Appl. Catal. B* 2018, **239**, 1-9.
- [10] H. Liu, P. Chen, X. Yuan, Y. Zhang, H. Huang, L. Wang, F. Dong, Pivotal roles of artificial oxygen vacancies in enhancing photocatalytic activity and selectivity on Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanosheets, *Chinese J. Catal.* 2019, **40**, 620-630.
- [11] Z. Zhao, Y. Cao, F. Dong, F. Wu, B. Li, Q. Zhang, Y. Zhou, The activation of oxygen through oxygen vacancies in BiOCl/PPy to inhibit toxic intermediates and enhance the activity of photocatalytic nitric oxide removal, *Nanoscale* 2019, **11**, 6360-6367.
- [12] J. Liao, L. Chen, M. Sun, B. Lei, X. Zeng, Y. Sun, F. Dong, Improving visible-light-driven photocatalytic NO oxidation over BiOBr nanoplates through tunable oxygen vacancies, *J. Catal.* 2018, **39**, 779-789.
- [13] G. Dong, L. Yang, F. Wang, L. Zang, C. Wang, Removal of Nitric Oxide through Visible Light Photocatalysis by g-C<sub>3</sub>N<sub>4</sub> Modified with Perylene Imides, *ACS Catal.*, 2016, **6**, 6511-6519.
- [14] K. Li, Wen Cui, J. Li, Y. Sun, Y. Chua, Guang. Jiang, Y. Zhou, Y. Zhang, F. Dong, Tuning the reaction pathway of photocatalytic NO oxidation process to control the secondary pollution on monodisperse Au nanoparticles@ g-C<sub>3</sub>N<sub>4</sub>, *Chem. Eng. J.*, 2019, **378**, 122184.

- [15] G. Jiang, J. Cao, M. Chen, X. Zhang, F. Dong, Photocatalytic NO oxidation on N-doped TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction: enhanced efficiency, mechanism and reaction pathway, *Appl. Surf. Sci.*, 2018, **458**, 77-85.
- [16] F. Dong, Y. Li, W. Ho, H. Zhang, M. Fu, Z. Wu, Synthesis of mesoporous polymeric carbon nitride exhibiting enhanced and durable visible light photocatalytic performance, *Chin. Sci. Bull.*, 2014, **59**, 688-698.
- [17] J. Yang, X. Zhu, Z. Mo, J. Yi, J. Yan, J. Deng, Y. Xu, Y. She, J. Qian, H. Xu, H. Li, A multidimensional In<sub>2</sub>S<sub>3</sub>-CuInS<sub>2</sub> heterostructure for photocatalytic carbon dioxide reduction, *Inorg. Chem. Front.* 2018, **5**, 3163-3169.
- [18] J. Lin, Z. Pan, X. Wang, Photochemical Reduction of CO<sub>2</sub> by Graphitic Carbon Nitride Polymers, *ACS Sustainable Chem. Eng.* 2014, **2**, 353-358.
- [19] C. Huang, C. Chen, M. Zhang, L. Lin, X. Ye, S. Lin, M. Antonietti, X. Wang, Carbon-doped BN nanosheets for metal-free photoredox catalysis, *Nat. Commun.* 2015, **6**, 7698.
- [20] Z. Mo, X. Zhu, Z. Jiang, Y. Song, D. Liu, H. Li, X. Yang, Y. She, Y. Lei, S. Yuan, H. Li, L. Song, Q. Yan, H. Xu, Porous nitrogen-rich g-C<sub>3</sub>N<sub>4</sub> nanotubes for efficient photocatalytic CO<sub>2</sub> reduction, *Appl. Catal., B* 2019, **256**, 117854.
- [21] L. Shi, T. Wang, H. Zhang, K. Chang, J. Ye, Electrostatic Self-Assembly of Nanosized Carbon Nitride Nanosheet onto a Zirconium Metal-Organic Framework for Enhanced Photocatalytic CO<sub>2</sub> Reduction, *Adv. Funct. Mater.* 2015, **25**, 5360-5367.
- [22] S. Sato, T. Morikawa, S. Saeki, T. Kajino, T. Motohiro, Visible-Light-Induced Selective CO<sub>2</sub> Reduction Utilizing a Ruthenium Complex Electrocatalyst Linked to a p-Type Nitrogen-Doped Ta<sub>2</sub>O<sub>5</sub> Semiconductor, *Angew. Chem. Int. Ed.* 2010, **49**, 5101-5105.
- [23] R. Kuriki, M. Yamamoto, K. Higuchi, Y. Yamamoto, M. Akatsuka, D. Lu, S. Yagi, T.

Yoshida, O. Ishitani, K. Maeda, Robust Binding between Carbon Nitride Nanosheets and a Binuclear Ruthenium(II) Complex Enabling Durable, Selective CO<sub>2</sub> Reduction under Visible Light in Aqueous Solution, *Angew. Chem. Int. Ed.* 2017, **56**, 4867-4871.

[24] Y. Zheng, L. Lin, X. Ye, F. Guo, X. Wang, Helical graphitic carbon nitrides with photocatalytic and optical activities, *Angew. Chem. Int. Ed.* 2014, **53**, 11926-11930.

[25] P. Li, Y. Zhou, Z. Zhao, Q. Xu, X. Wang, M. Xiao, Z. Zou, Hexahedron Prism-Anchored Octahedral CeO<sub>2</sub>: Crystal Facet-Based Homojunction Promoting Efficient Solar Fuel Synthesis, *J. Am. Chem. Soc.* 2015, **137**, 9547-9550.

[26] B. AlOtaibi, S. Fan, D. Wang, J. Ye, Z. Mi, Wafer-Level Artificial Photosynthesis for CO<sub>2</sub> Reduction into CH<sub>4</sub> and CO Using GaN Nanowires, *ACS Catal.* 2015, **5**, 5342-5348.

[27] R. Li, J. Hu, M. Deng, H. Wang, X. Wang, Y. Hu, H. Jiang, J. Jiang, Q. Zhang, Y. Xie, Y. Xiong, Integration of an inorganic semiconductor with a metal-organic framework: a platform for enhanced gaseous photocatalytic reactions, *Adv. Mater.* 2014, **26**, 4783-4788.

[28] W. Tu, Y. Zhou, Q. Liu, S. Yan, S. Bao, X. Wang, M. Xiao, Z. Zou, An In Situ Simultaneous Reduction-Hydrolysis Technique for Fabrication of TiO<sub>2</sub>-Graphene 2D Sandwich-Like Hybrid Nanosheets: Graphene-Promoted Selectivity of Photocatalytic-Driven Hydrogenation and Coupling of CO<sub>2</sub> into Methane and Ethane, *Adv. Funct. Mater.* 2013, **23**, 1743-1749.