

## Supporting Information

### Interfacial Engineering by Creating Cu-Based Ternary Heterostructures on C<sub>3</sub>N<sub>4</sub> Tubes towards Enhanced Photocatalytic Oxidative Coupling of Benzylamines

Yunqi Fu,<sup>a</sup> Mang Zheng,<sup>a</sup> Qi Li,<sup>a</sup> Liping Zhang,<sup>b,\*</sup> Shuai Wang,<sup>c,\*</sup> V.V. Kondratiev<sup>d</sup>,  
Baojiang Jiang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China.

<sup>b</sup> Department of Chemistry and Biochemistry, Kent State University, Kent, OH 44242, USA

<sup>c</sup> Department of Food and Environment Engineering, Heilongjiang East University, Harbin, China

<sup>d</sup> Institute of Chemistry, Saint Petersburg State University, Russia.

E-mail: Lzhang30@kent.edu; 79652283@qq.com; jbj@hlju.edu.cn; jiangbaojiang88@sina.com

**Table S1.** Cu contents for different photocatalysts determined by inductively coupled plasma spectrometer (ICP).

Sample	Cu content (%)
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -1	66.46
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -2	60.48
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -3	59.19
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -4	33.47

**Table S2.** Elemental analysis results of different photocatalysts.

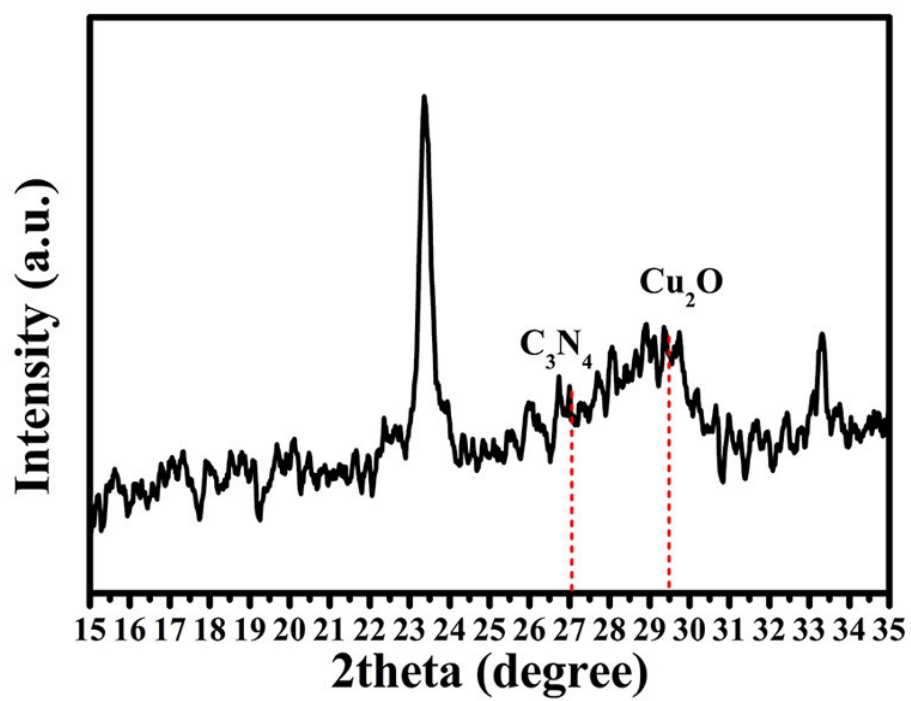
Sample	C (%)	N (%)	C/N
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -1	5.32	8.63	0.6165
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -2	6.52	10.90	0.5982
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -3	11.8	20.46	0.5767
Cu/Cu <sub>2</sub> O/Cu <sub>3</sub> N/C <sub>3</sub> N <sub>4</sub> -4	9.10	15.07	0.6038

**Table S3.** Results of benzylamine oxidation coupling induced by Cu/Cu<sub>2</sub>O/Cu<sub>3</sub>N/C<sub>3</sub>N<sub>4</sub>-3 under different reaction conditions.

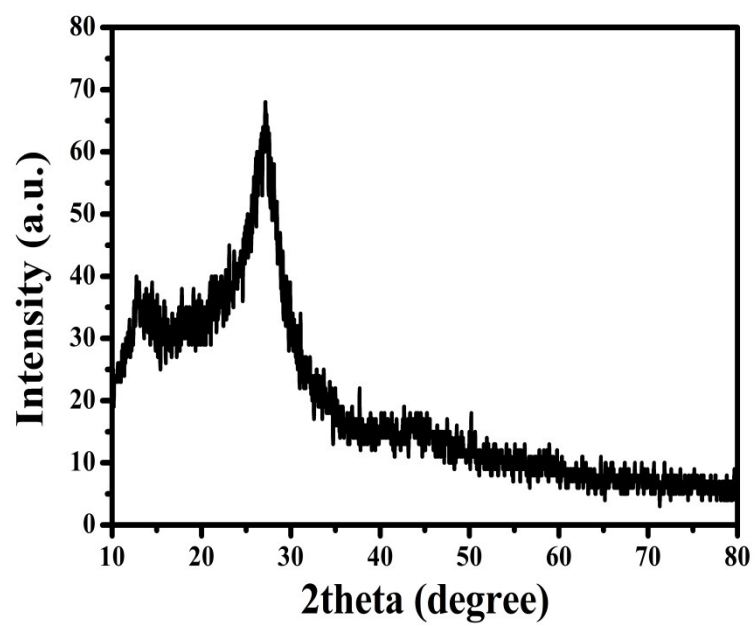
Condition	Conversion	Selectivity
Thermal (50°C)	33%	94%
Illumination	74%	98%
Photo-thermal	99%	98%

**Table S4.** Benzylamine oxidation coupling induced by Cu/Cu<sub>2</sub>O/Cu<sub>3</sub>N/C<sub>3</sub>N<sub>4</sub>-3 under different atmospheres.

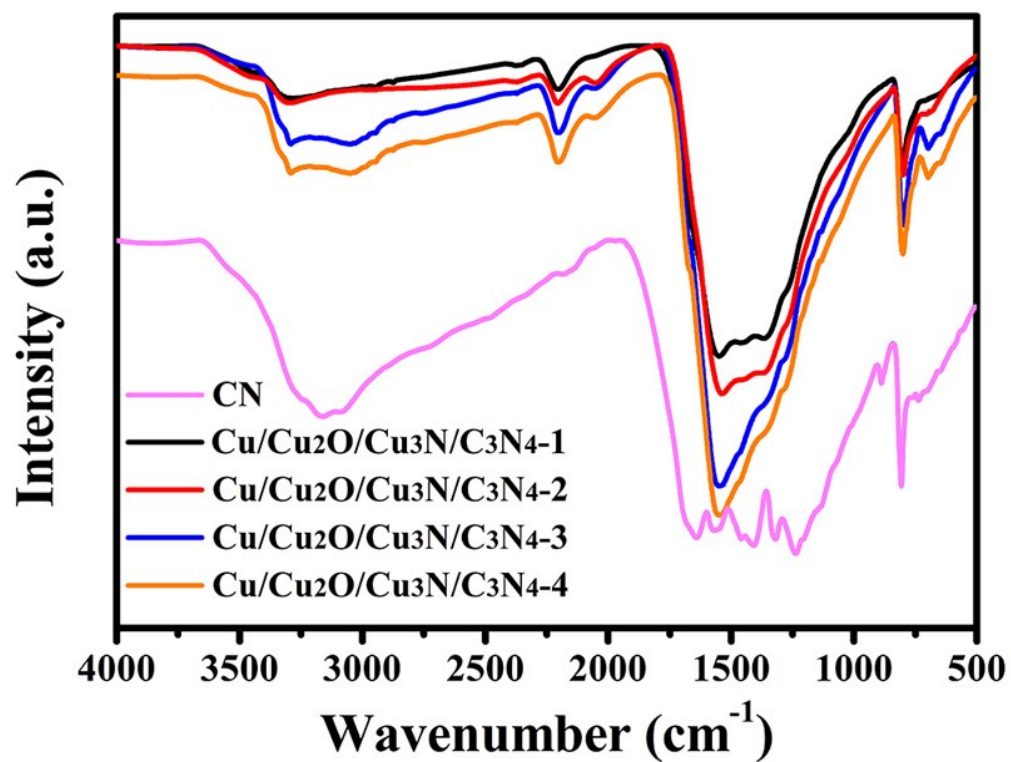
Condition	Conversion	Selectivity
N <sub>2</sub>	44%	98%
O <sub>2</sub>	98%	95%
Air	99%	98%



**Figure S1.** XRD partial enlarged view of Cu/Cu<sub>2</sub>O/Cu<sub>3</sub>N/C<sub>3</sub>N<sub>4</sub>-3.

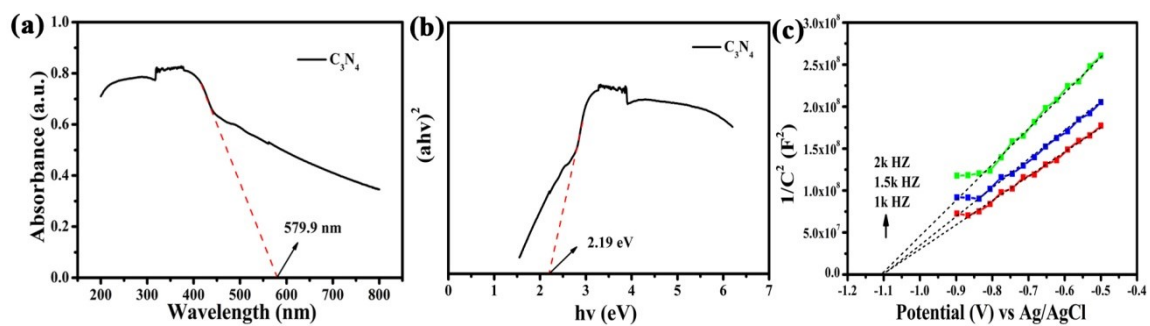


**Figure S2.** XRD pattern of the sample without adding copper acetate.

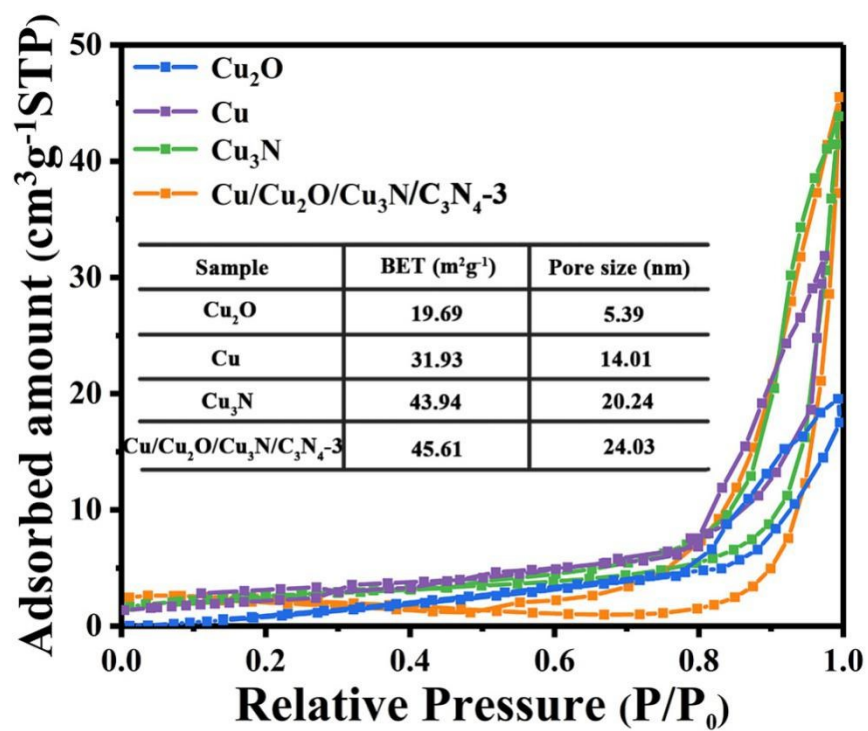


**Figure S3.** Fourier transform infrared spectrum of bulk carbon nitride and Cu/Cu<sub>2</sub>O/Cu<sub>3</sub>N/C<sub>3</sub>N<sub>4</sub> of different molar ratio.

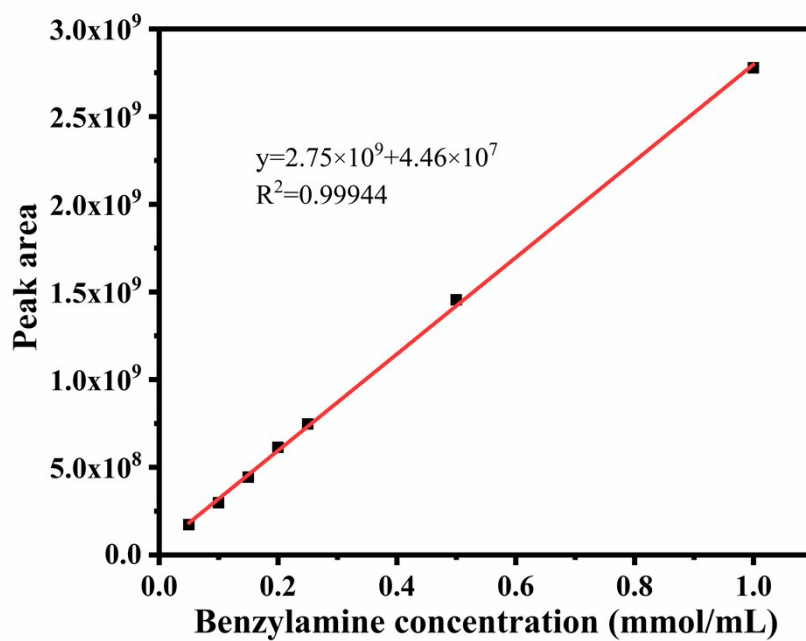




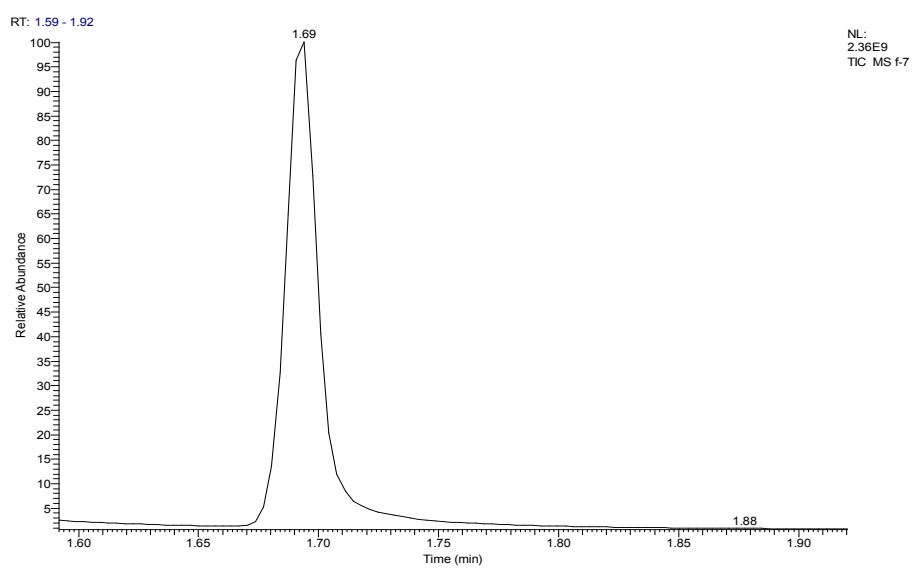
**Figure S4.** (a) Diffuse reflectance spectra (DRS) and (b) Tauc plots of  $C_3N_4$ . (c) Mott-Schottky plots of  $C_3N_4$  at various frequencies (pH = 7).



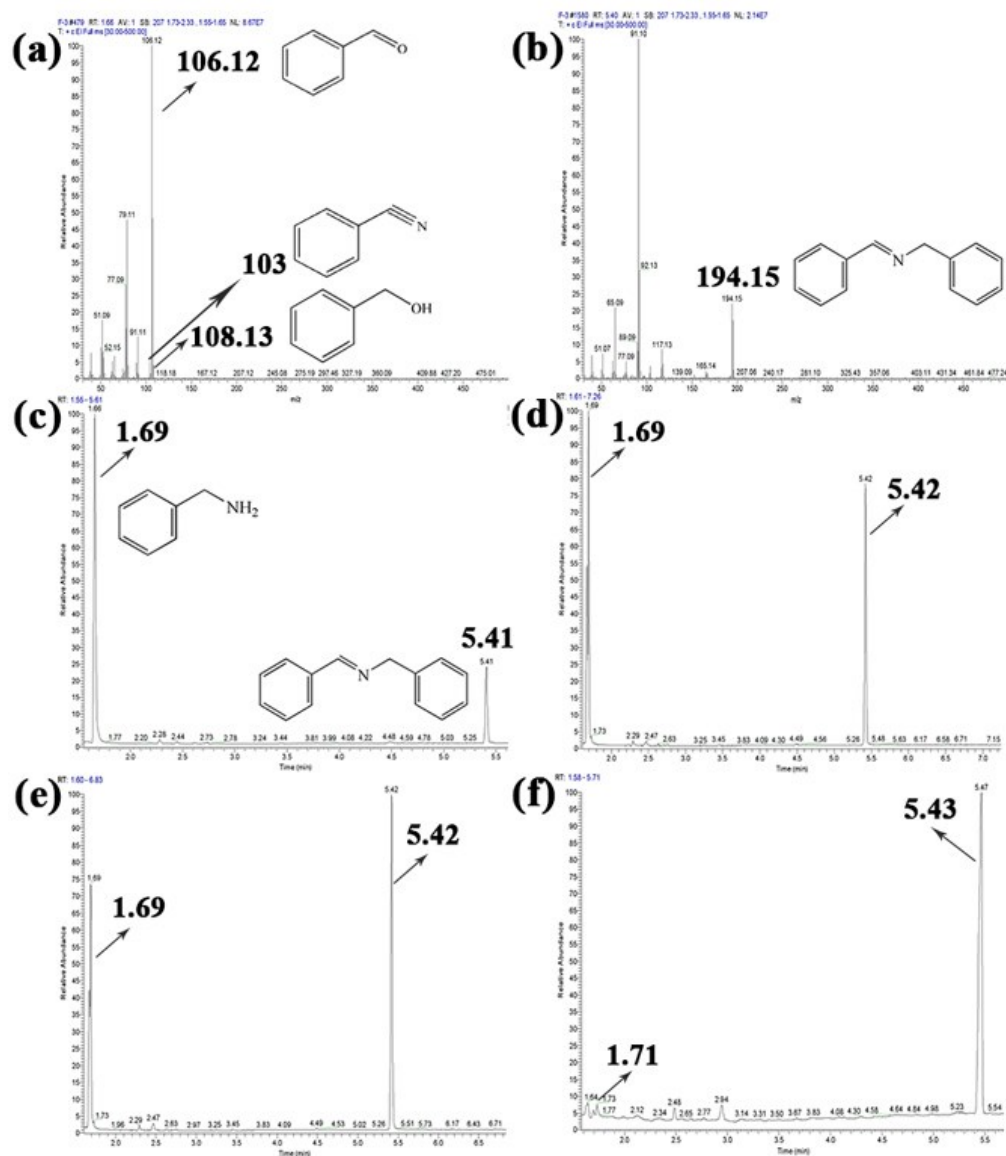
**Figure S5.** Nitrogen adsorption-desorption isotherms of Cu<sub>2</sub>O, Cu, Cu<sub>3</sub>N and Cu/Cu<sub>2</sub>O/Cu<sub>3</sub>N/C<sub>3</sub>N<sub>4</sub>-3. The inserted table shows the BET surface area and pore size.



**Figure S6.** Standard calibration curve of benzylamine for gas chromatography.



**Figure S7.** Chromatogram of chromatographic grade benzylamine.



**Figure S8.** (a) Mass spectra of benzylamine and (b) imine at the 3<sup>rd</sup> hour of reaction. Chromatograms of the benzylamine coupling reaction at (c) 3<sup>rd</sup> hour, (d) 6<sup>th</sup> hour, (e) 9<sup>th</sup> hour and (f) 12<sup>th</sup> hour.