Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

for

Facile formation of CoN_4 active sites onto SiO_2 support to achieve robust CO_2 and protons reduction in a noble-metal-free photocatalytic system

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1. Chemicals

Tetraethylorthosilicate (TEOS), γ-aminopropyltrimethoxysilane (APTMS), triethylamine, ammonium hydroxide ($NH_3 \cdot H_2O$, 25%-28%), triethylamine (TEA) and cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) were purchased from commercial suppliers (Sinopharm chemical reagent co., LTD, Adamas and Sigma-Aldrich) and used without further purification. CO_2 (99.999%), CO (99.999%), CH_4 (99.99%) were purchased from commercial supplier (Huaerwen). $^{13}CO_2$ (99% ^{13}C atom) were purchased from Aldrich. All solvents of analytical grade were purchased from commercial suppliers and used without further purification. ***g*-C_3N_4:** *g*-C_3N_4 were synthesized according to previously reported procedures by heating approximately 5 g of melamine at a rate of 5 K min^{-1} to 823 K and then maintaining this temperature for another 2 h.

2. X-Ray diffraction pattern of *g*-C_3N_4

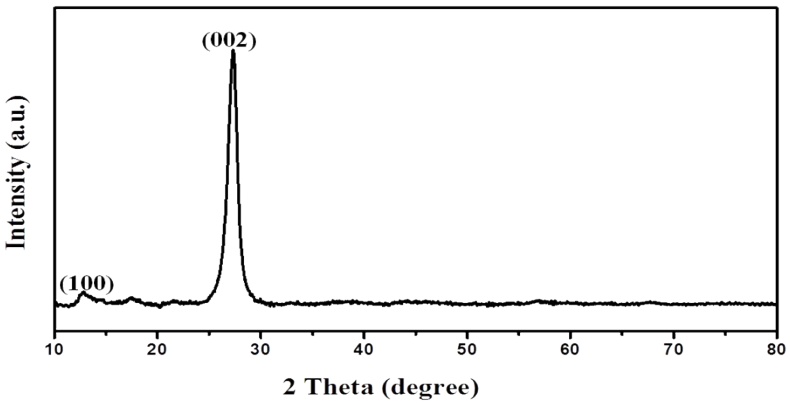

Figure S1. X-Ray diffraction spectrum of *g*-C_3N_4.

3. UV-vis diffuse reflectance spectrum of *g*-C_3N_4

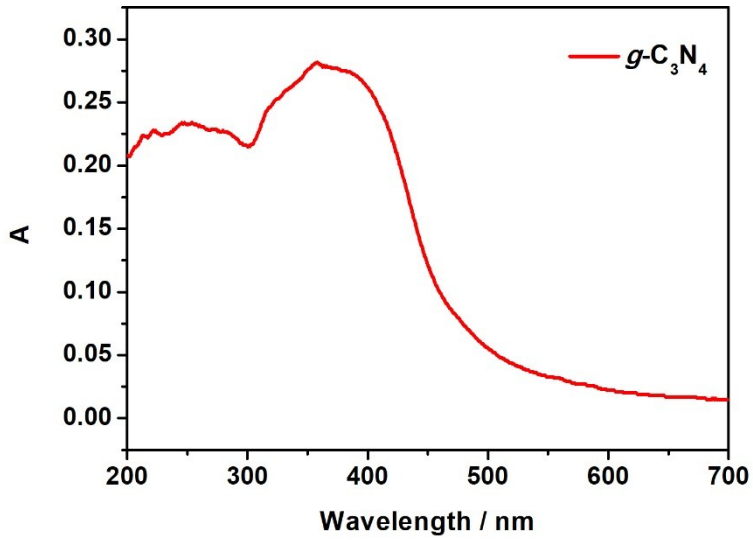

Figure S2. UV-vis diffuse reflectance spectrum of *g*-C_3N_4

4. UV-vis diffuse reflectance spectra of raw SiO_2, NH_2-SiO_2 and CoN_4-SiO_2

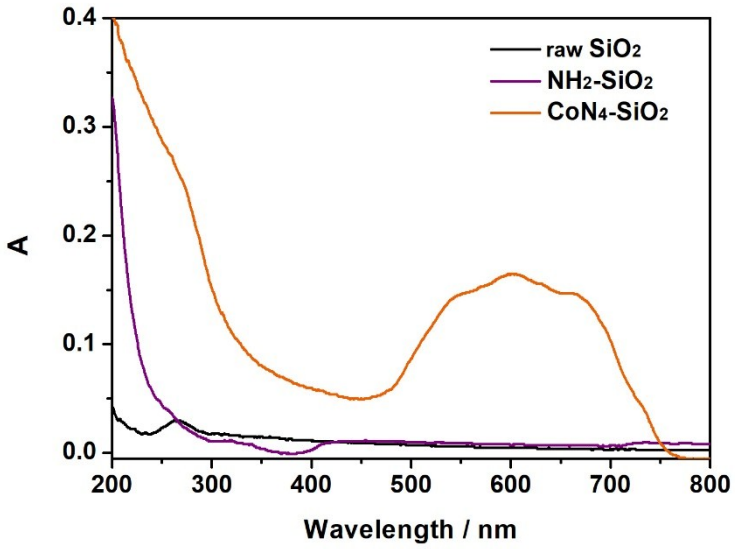

Figure S3. UV-vis diffuse reflectance spectra (DRS) of raw SiO_2, NH_2-SiO_2, and **CoN_4-SiO_2**

5. IR spectra

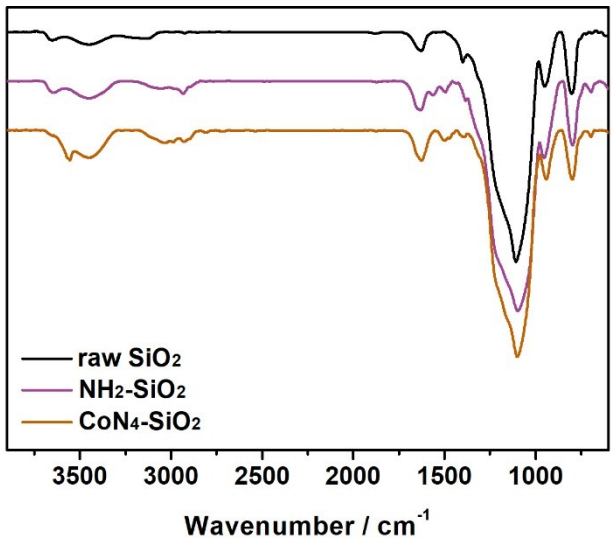

Figure S4. IR spectra of raw SiO_2, NH_2-SiO_2, and **CoN_4-SiO_2**

6. XPS spectra

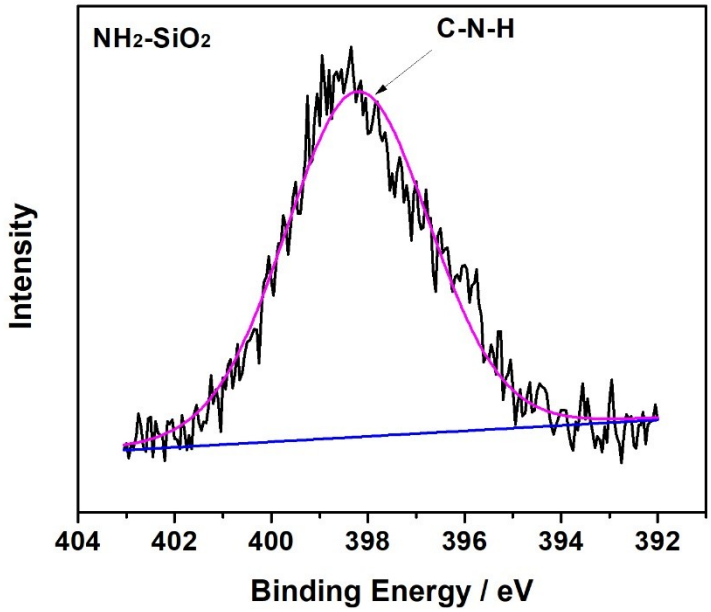

Figure S5. XPS spectrum of *N* 1s of NH_2-SiO_2

7. Photocatalytic syngas production in CH_3CN

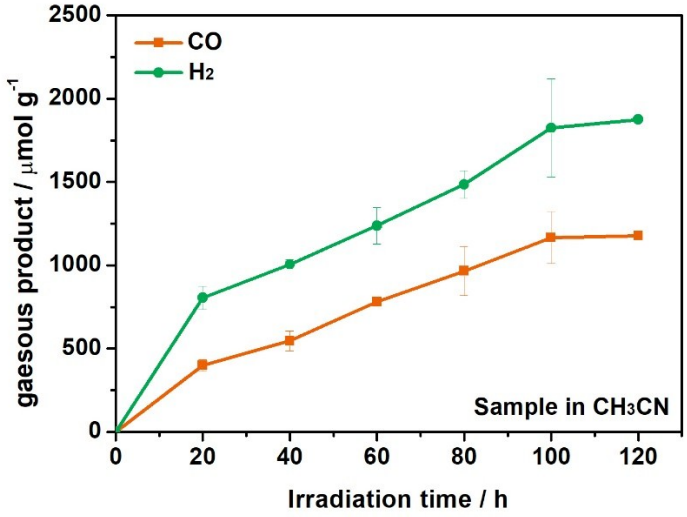

Figure S6. Long-time photocatalysis in CO_2-saturated CH_3CN; samples composition: **CoN_4-SiO_2** (5.00 mg), *g*-C_3N_4 (10.00 mg), TEA (1.00 mL), total volume = 5.00 mL. The sample was irradiated under visible light (Blue LED, λ_{max} = 450 nm).

8. Emission spectra of *g*-C_3N_4 in the presence of TEA

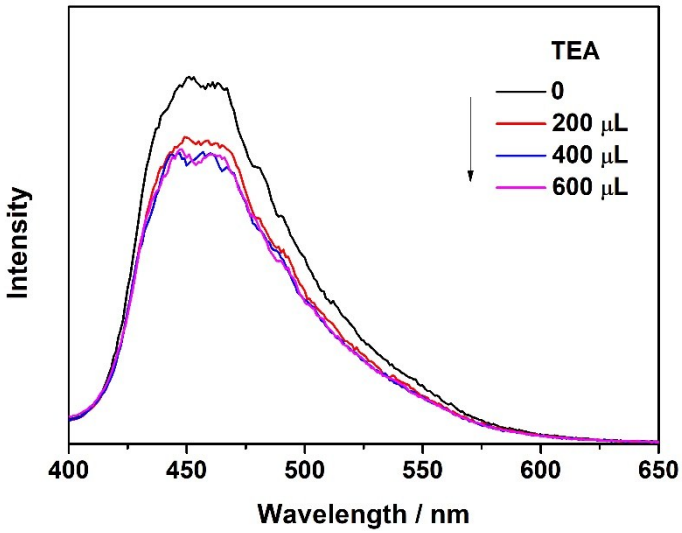

Figure S7. Emission spectra of *g*-C_3N_4 in CH_3CN in the absence and presence of NH_2-SiO_2 (up) or TEA (bottom) (excitation wavelength = 380 nm).

9. Comparison of the reported heterogeneous photocatalytic syngas production systems

Table S1. Comparison of the reported heterogeneous photocatalytic syngas production systems

No.	Catalyst / Photocatalyst	Photosensitizer	*n*(CO) [μmol]	*n*(H_2) [μmol]	CO/H_2 *ratio*	*n/m* (CO) [μmol·g^{-1}]	*n/m* (H_2) [μmol·g^{-1}]	*Lifetime* [h]	Ref.
1[a]	**CoN_4-SiO_2**	*g*-C_3N_4	11.34	13.93	1.0 : 1.2	2267	2786	140	This work
2[b]	**CoN_4-SiO_2**	*g*-C_3N_4	5.89	9.38	1.0 : 1.6	1178	1875	120	This work
4	ReP + CoP/Dye/TiO_2	-	7.73	2.21	3.5 : 1.0	773	221	10	[c]
5	Rh(PD)Au@STO	-	138.45	26.03	5.3 : 1.0	1846	347	5	[d]

[a]. In CH_3CN/H_2O ($v(H_2O)$ = 100 μL, total volume = 5.00 mL)

[b]. In CH_3CN (total volume = 5.00 mL)

[c]. J.-S. Lee, D.-I. Won, W.-J. Jung, H.-J. Son, C. Pac, S. O. Kang, *Angewandte Chemie-International Edition* **2017**, *56*, 976-980.

[d]. D. Li, S. Ouyang, H. Xu, D. Lu, M. Zhao, X. Zhang, J. Ye, *Chem. Commun.* **2016**, *52*, 5989-5992.