

Supporting Information

N-doped rutile TiO₂ nanorod@g-C₃N₄ core/shell S-scheme heterojunction for boosting photoreduction CO₂ activity

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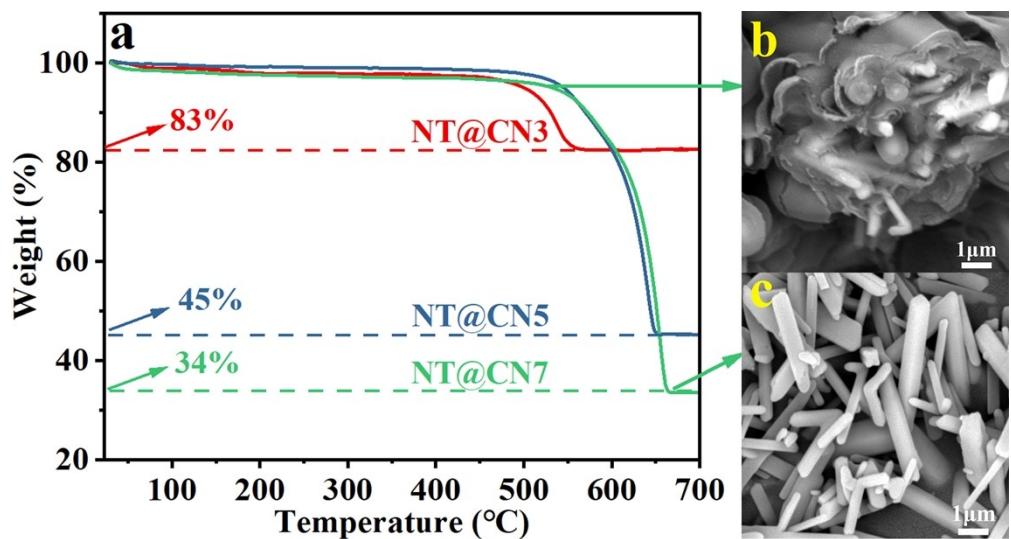


Figure S1. (a) TG curves of NT@CN3, NT@CN5, and NT@CN7. SEM images of NT@CN7 before (b) and after (c) thermogravimetric analysis.

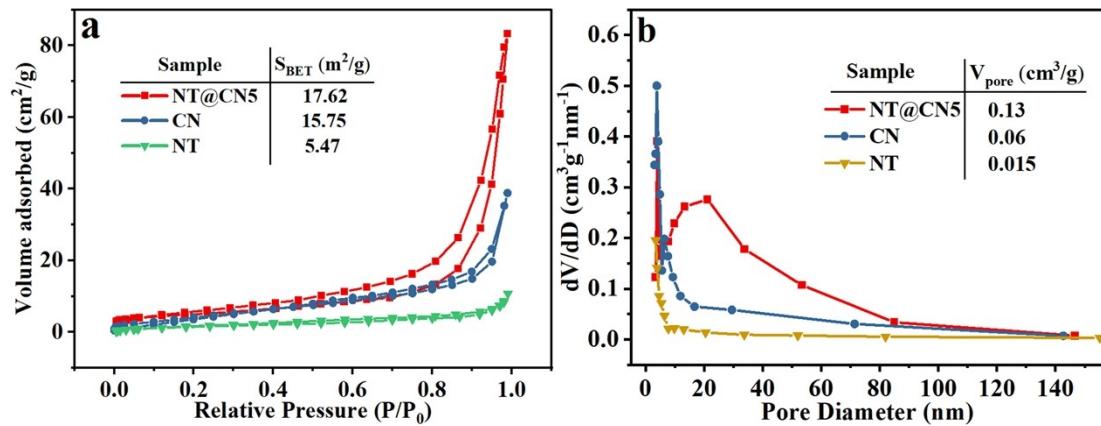


Figure S2. N₂ adsorption-desorption isotherms (a) and corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution plots (b) of NT, CN, and NT@CN5 samples.

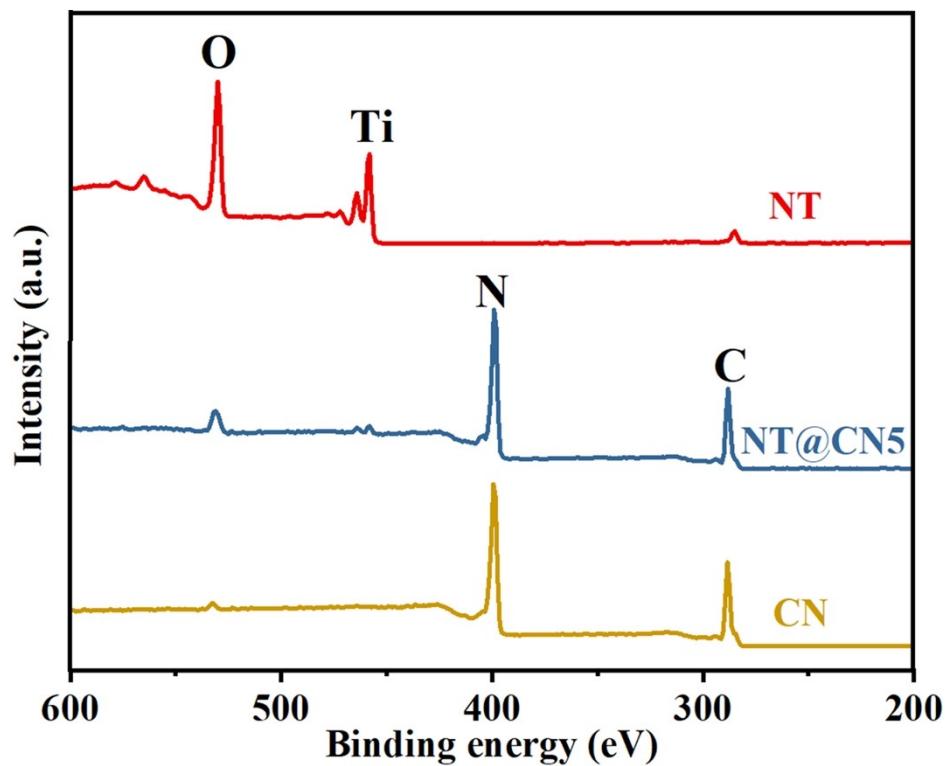


Figure S3. XPS survey spectra of CN, NT, and NT@CN5.

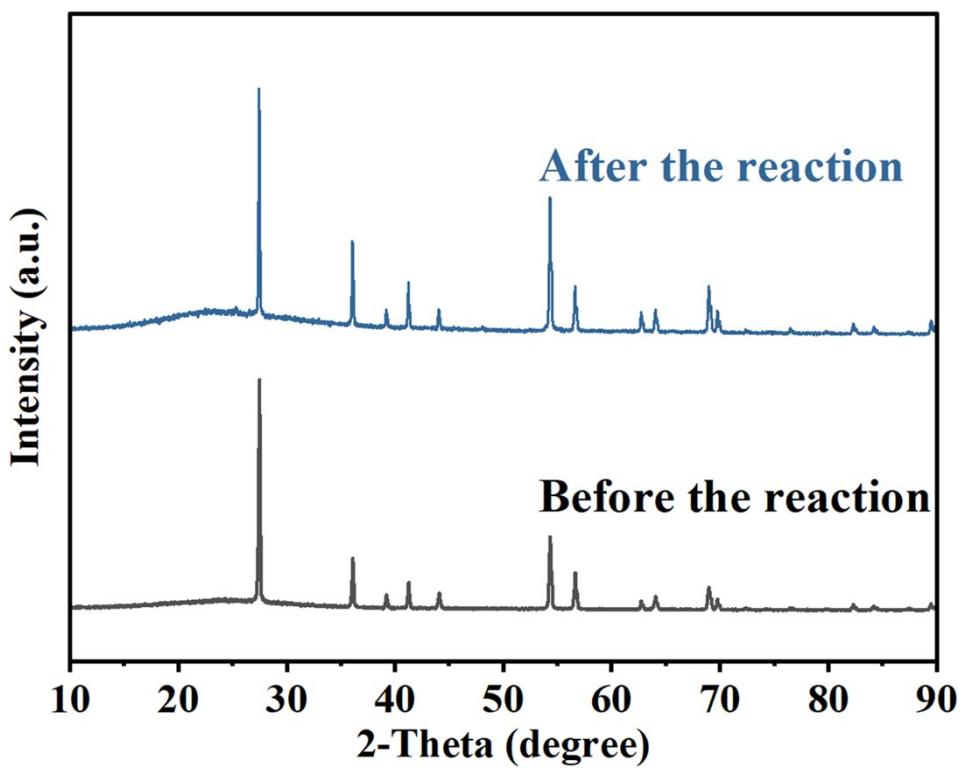


Figure S4. XRD patterns of as-prepared NT@CN5 before and after reaction.

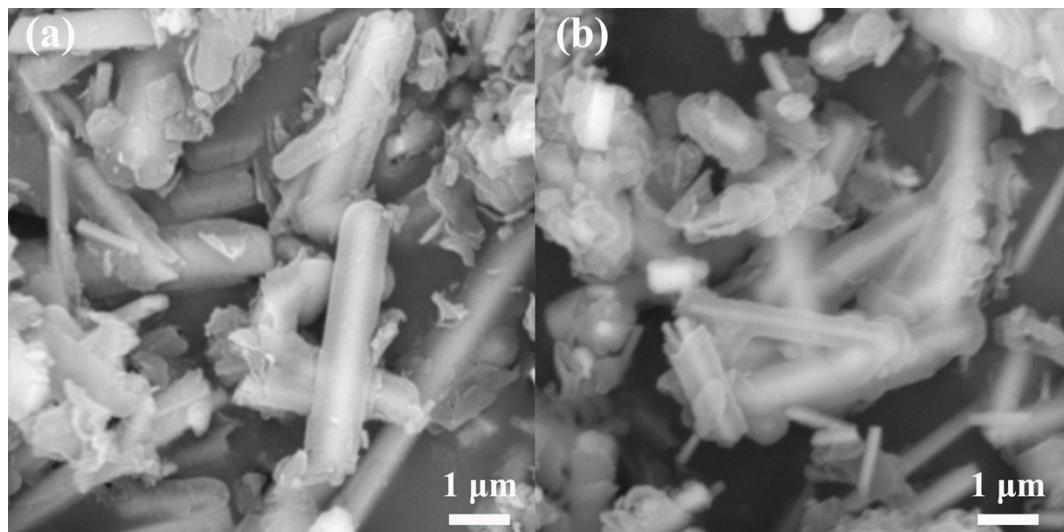


Figure S5. SEM images of as-prepared NT@CN5 before (a) and after (b) reaction.

Table S1. Photocatalytic CO production on NT@CN5 sample, compared with reported data for other photocatalysts.

Photocatalyst	Reaction conditions	Reaction time (h)	CO Production ($\mu\text{mol g}^{-1}\text{h}^{-1}$)	Reference
A-TiO ₂ /R-TiO ₂ (Anatase and Rutile)	300 W Hg-Xe, liquid phase (0.1 M KHCO ₃ aqueous solution), 100 mg catalyst	5	1.39	S1
TiO ₂ /g-C ₃ N ₄ nanosheet (Anatase)	150 W Xe, $\lambda>325$ nm, gas phase, 25 mg catalyst	6	2.04	S2
TiO ₂ nanosheets- {001} (Anatase)	2x18W Hg, $\lambda=245$ nm, liquid phase (2 M NaOH aqueous solution), 300 mg catalyst	5	0.12	S3
TiO ₂ -CoO _x (Anatase)	150 W UV, $\lambda=365$ nm, gas phase, 50 mg catalyst, 120 °C	5	1.24	S4
Au/TiO ₂ (Anatase)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase	6	0.3	S5
AuPd ₃ /TiO ₂ (Anatase)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase	6	2.6	S5
Pd/TiO ₂ (Anatase)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase	6	3.9	S5
g-C ₃ N ₄ /TiO ₂ - {210} cubes (Brookite)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase, 60 mg catalyst	2	1.27	S6
I/TiO ₂ -{001} (Anatase)	500 W Xe, $\lambda=320\text{-}780$ nm, gas phase, 0.3 g catalyst	6	3.43	S7
TiO ₂ (P25)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase, 100 mg catalyst	5	1.84	S8
PdS QD-Cu/TiO ₂	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase	6	0.82	S9
I doped TiO ₂	450 W Xe, $\lambda=320\text{-}780$ nm, gas phase, 200 mg catalyst	3	2.4	S10
N-doped rutile TiO ₂ @g-C ₃ N ₄ (Rutile)	300 W Xe, $\lambda=320\text{-}780$ nm, gas phase, 50 mg catalyst, 80 kPa,	5	6.67	this work

Table S2. Decay parameters and average lifetime according to a biexponential fitting model of the PL decay curves.

Sample	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	τ_{ave} (ns)
NT	11.02	1.95	0.41	7.99	6.36
CN	6.76	2.33	0.44	11.71	11.36
NT@CN5	6.62	2.2	0.31	15.32	14.28

References

- [S1] Akrami S, Watanabe M, Ling TH, et al. High-pressure TiO_2 -II polymorph as an active photocatalyst for CO_2 to CO conversion, *Appl. Catal. B.* 298 (2021) 120566.
- [S2] Crake A, Christoforidis KC, Godin R, et al. Titanium dioxide/carbon nitride nanosheet nanocomposites for gas phase CO_2 photoreduction under UV-visible irradiation, *Appl. Catal. B.* 242 (2019) 369-378.
- [S3] He Z, Wen L, Wang D, et al. Photocatalytic reduction of CO_2 in aqueous solution on surface-fluorinated anatase TiO_2 nanosheets with exposed {001} facets, *Energy Fuels.* 28(6) (2014) 3982-3993.
- [S4] Li Y, Wang C, Song M, et al. $\text{TiO}_{2-x}/\text{CoO}_x$ photocatalyst sparkles in photothermocatalytic reduction of CO_2 with H_2O steam, *Appl. Catal. B.* 243 (2019) 760-770.
- [S5] Jiao J, Wei Y, Zhao Y, et al. AuPd/3DOM- TiO_2 catalysts for photocatalytic reduction of CO_2 : High efficient separation of photogenerated charge carriers, *Appl. Catal. B.* 209(228-239) (2017) 228.
- [S6] Li K, Peng B, Jin J, et al. Carbon nitride nanodots decorated brookite TiO_2 quasi nanocubes for enhanced activity and selectivity of visible-light-driven CO_2 reduction, *Appl. Catal. B.* 203 (2017) 910-916.
- [S7] He Z, Yu Y, Wang D, et al. Photocatalytic reduction of carbon dioxide using iodine-doped titanium dioxide with high exposed {001} facets under visible light, *RSC Adv.* 6(28) (2016) 23134-23140.
- [S8] Wang Y, Chen Y, Zuo Y, et al. Hierarchically mesostructured TiO_2 /graphitic carbon composite as a new efficient photocatalyst for the reduction of CO_2 under simulated solar irradiation, *Catal. Sci. Technol.* 3(12) (2013) 3286-3291.
- [S9] Wang C, Thompson RL, Ohodnicki P, et al. Size-dependent photocatalytic reduction of CO_2 with PbS quantum dot sensitized TiO_2 heterostructured photocatalysts, *J. Mater. Chem.* 21(35) (2011) 13452-13457.
- [S10] Zhang Q, Li Y, Ackerman EA, et al. Visible light responsive iodine-doped TiO_2 for photocatalytic reduction of CO_2 to fuels, *Appl. Catal. A-Gen.* 400(1-2) (2011) 195-202.