

Supporting Information

Enhanced Quantum Yield of Nitrogen Fixation for Hydrogen Storage with In-Situ-Formed Carbonaceous Radicals

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1. Experimental details

Materials

5,5-Dimethyl-1-pyrroline N-oxide (DMPO, GR) and 2,9-dimethyl-1,10-phenanthroline (DMP, AR) are purchased from Sigma Chemicals (America). All other chemicals used here are of analytical grade and purchased from Sinopharm Chemicals (China). The chemicals are used as received.

β -Ga₂O₃ is prepared using a method previously optimized in our laboratory with polyethylene glycol as a template.^[1]

Activity test and methods

Nitrogen photofixation for hydrogen storage was carried out in a double walled cylindrical quartz reactor with a water circulation facility. 0.1 g of nanostructured β -Ga₂O₃ was mixed with 100 mL of solution containing 0.02 mol L⁻¹ hole scavengers. Methanol, ethanol, *n*-propanol, *n*-butanol, and *t*-butanol (TBA) were chosen as hole scavengers, respectively. The mixture was stirred homogeneously in dark and then irradiated with photons from an 8 W UV lamp (254 nm). Samples were taken out every 30 min and filtered through a porous membrane (0.45 μ m).

To exclude the adsorption effect of β -Ga₂O₃, a certain concentration of NH₃•H₂O was added to the

100 mL mixture and stirred without illumination and sampled every 30 min to track changes of NH₃ concentration. To study the effect of different atmosphere, the mixture with 0.02 mol L⁻¹ TBA was purged with different gases (4:1 N₂/O₂, or 4:1 N₂/Ar) for 2 h and sealed.

The concentration of NH₃, NO₃⁻, NO₂⁻, N₂H₄, and H₂O₂ was determined colorimetrically by a UV-Vis spectrophotometer (TU-1901, China) with a precision of ± 5%. NH₃ was detected using Nessler's reagent as a chromogenic agent at 420 nm. NO₂⁻ was detected using p-aminobenzene sulfonamide and *N*-(1-naphthyl) ethylenediamine dihydrochloride at 540 nm. N₂H₄ was detected using 4-Dimethylaminobenzaldehyde at 458 nm. H₂O₂ was detected using copper(II) ion and 2,9-dimethyl-1,10-phenanthroline (DMP) under 454 nm. NO₃⁻ was determined by dual wavelength spectrophotometry at 220 and 275 nm, respectively.

It is worth mentioning that blank experiments in the absence of β-Ga₂O₃, hole scavengers or UV source were also performed and no ammonia was detected, and that adsorption capacity of the catalyst for ammonia was essentially negligible (Data not shown), and that no NO₃⁻ or NO₂⁻ was detected within 3 h. The concentration of ammonia detected in solution could represent the total amount that produced from N₂ in the systems.

The quantum yield was calculated as follow:^[2]

$$\phi = \frac{3k}{I} \quad (S1)$$

Where *k* is the generation rate of NH₃, *I* is the absorption rate of photo-generated electrons, which is 7.06 × 10⁻⁶ Einstein s⁻¹ measured by a UV meter (ST-512, China) and corrected with permanganometric method.

Characterizations

Mott-Schottky plot was recorded with a three-electrode electrochemical analyzer system (CHI650D, China). The electrolytic solution was composed of 0.4 mol L⁻¹ KNO₃ and 5 × 10⁻⁶ mol L⁻¹ of K₃[Fe(CN)₆]. Before the test, the solution was purged with pure N₂ for 15 min to remove oxygen. Mott-Schottky equation is as follow:^[2-3]

$$C^{-2} = \left(\frac{2}{\varepsilon \varepsilon_0 q N_d} \right) \left(E - V_{fb} - \frac{kT}{q} \right) \quad (S2)$$

Where q is the electric charge; ε is the dielectric constant of the β -Ga₂O₃; ε_0 is the vacuum permittivity; k is Boltzmann's constant; V_{fb} is the flat band potential; N_d is the carriers in the semiconductors; E is the bias voltage relative to the reference electrode. Value of kT/q can be negligible. Therefore, we can obtain the flat band potential (V_{fb}) from the x-axis intercept of the linear.

ESR analysis was conducted with a Bruker model spectrometer (A300, Germany) with UV light of 254 nm. The following was the settings: centre field, 3512.0 G; microwave frequency, 9.683 GHz; and power, 20.24 mW. DMPO was used as radical capture agent. ESR spectra of β -Ga₂O₃ in dark and under UV were recorded. •OH is captured by 0.05 mol L⁻¹ DMPO using water as a solvent, while •O₂⁻ is detected in methanol. •CO₂⁻ in solutions with 0.02 mol L⁻¹ TBA or CH₃OH as hole scavenger was captured by 0.8 mol L⁻¹ DMPO.

Intermediate products were determined with a nano-liquid-chromatography electrospray ionization quadrupole time-of-flight mass spectrometer (Q-TOF-MS, MS4-APIQSTAR). The following was the settings: entrance voltage, 2500 V; drying gas, 350 °C nitrogen; spray rate, 4 L min⁻¹; injection volume, 50 µL; and injection flow rate, 25 µL min⁻¹. All intermediates were tested under positive ion mode. The minimum detection limit was 5 amu. Q-TOF-MS spectra of samples after reaction of 3 h containing TBA were recorded.

Density functional theory (DFT) calculations were performed with CASTEP module of Materials Studio (Accelrys Inc.). (111) facets of β -Ga₂O₃ were selected to build cells. And a 2×2 supercell was used as a calculation unit. A vacuum layer of 15 Å thicknesses was set above the crystal surface to prevent interactions between absorbed molecules and cell surface. GGA (the generalized gradient approximation) and PBE (Perdew, Burke, and Ernzerhof) were chosen as functions with a 340 eV energy cutoff and a $2 \times 3 \times 1$ *k*-grid.

2. Figure and table supplement

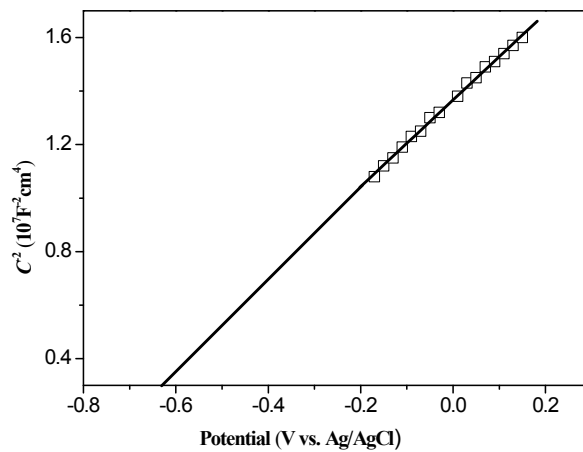


Fig. S1 Mott-Schottky plot of β -Ga₂O₃.

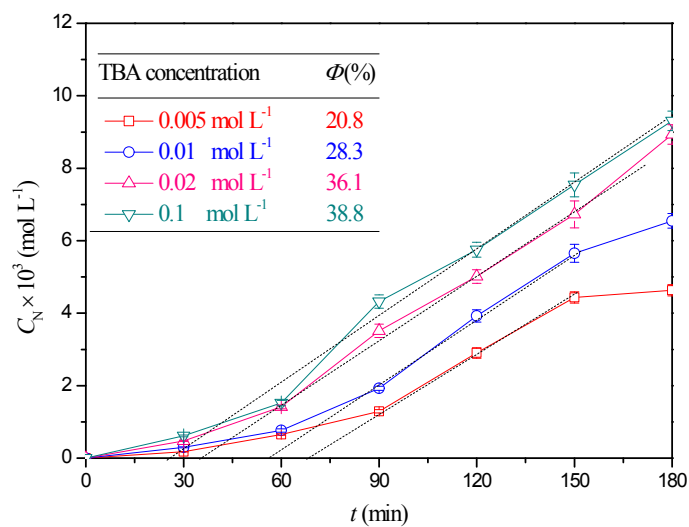


Fig. S2 Effect of TBA concentrations on photocatalytic hydrogen storage with β -Ga₂O₃ under irradiation of 254 nm at pH 7 and 25 °C.

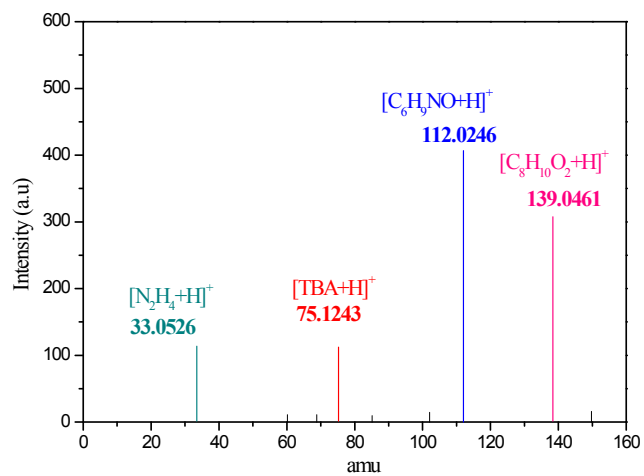


Fig. S3 Q-TOF-MS spectra of intermediates distribution in liquid sample after 3 h reaction.

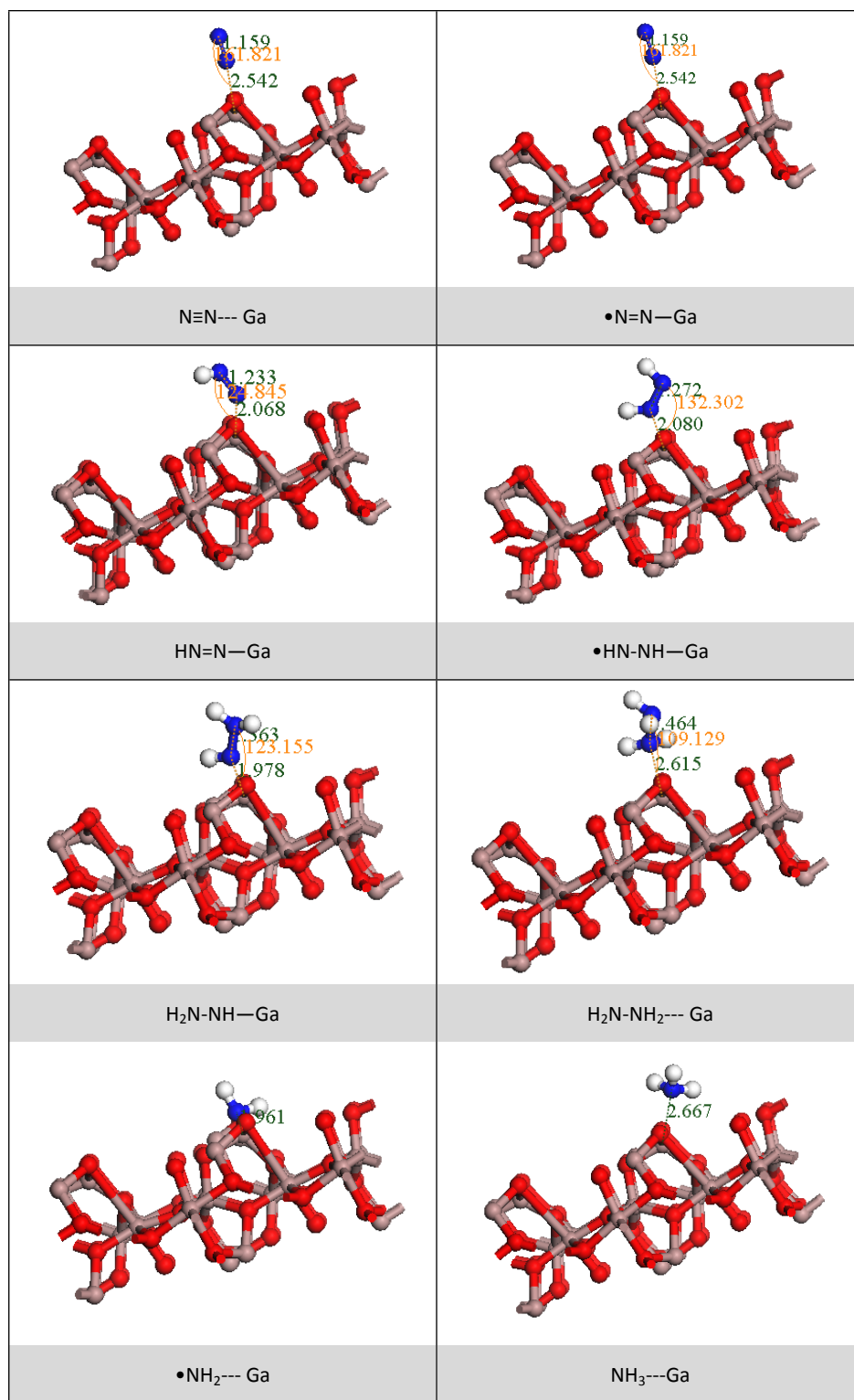


Fig. S4 Optimized structures of different adsorbate molecules calculated by DFT. Oxygen, red balls; gallium, pale pinkish grey balls; nitrogen, blue balls; and hydrogen, white balls.

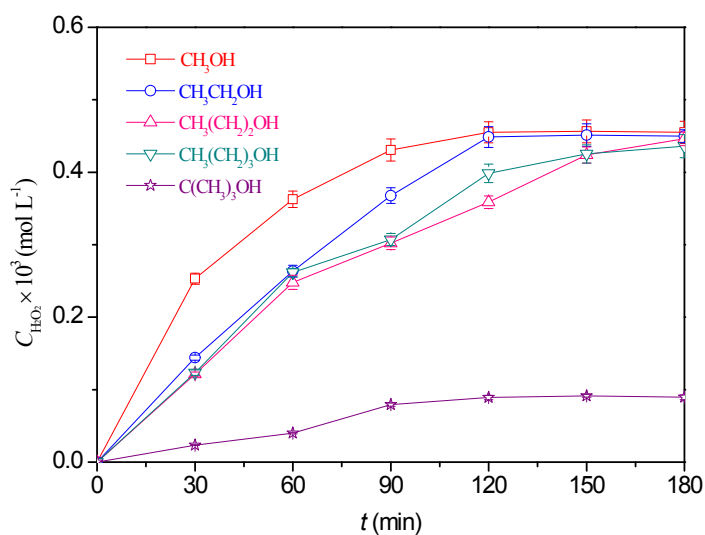


Fig. S5 Formation of H₂O₂ in 100 mL 0.02 mol L⁻¹ alcohol hole scavengers under irradiation of 254 nm at pH 7 and 25 °C.

Table S1. E_{HOMO} , Quantum yield, and kinetic parameters with different hole scavengers

Alcohol scavenger	Molecular	Quantum	Turnover efficiency	Reaction rate
	orbital energy	yield	(TOF)	$k(\text{NH}_3\text{-N})$
	E_{HOMO} (eV)	Φ (%)	($\mu\text{mol g}^{-1} \text{s}^{-1}$)	($\mu\text{mol L}^{-1} \text{s}^{-1}$)
CH ₃ OH	-13.776	12.5	2.95	0.295
CH ₃ CH ₂ OH	-13.700	4.35	1.02	0.102
CH ₃ (CH ₂) ₂ OH	-13.698	3.19	0.752	0.0752
CH ₃ (CH ₂) ₃ OH	-13.696	2.10	0.493	0.0493
C(CH ₃) ₃ OH	-13.311	36.1	8.51	0.851

Table S2. Optimized structure parameters of different intermediate states of nitrogen fixation process on (111) facets of β -Ga₂O₃

Mode	N-Ga distance (Å)	N-N distance (Å)	N-N-Ga angle (°)	Adsorption energy ΔE (eV)
N≡N---Ga	2.542	1.159	161.821	-0.975
•N=N—Ga	2.542	1.159	161.821	-0.975
HN=N—Ga	2.068	1.233	124.845	-1.848
•HN-NH—Ga	2.08	1.272	132.302	-2.044
H ₂ N-NH—Ga	1.978	1.363	123.155	-2.855
H ₂ N-NH ₂ ---Ga	2.615	1.464	109.129	-2.843
•NH ₂ ---Ga	1.961			-5.104
NH ₃ ---Ga	2.667			-2.525

Reference:

- [1] W. Zhao, Y. Yang, R. Hao, F. Liu, Y. Wang, M. Tan, J. Tang, D. Ren, D. Zhao, *J. Hazard. Mater.* **2011**, *192*, 1548-1554.
- [2] W. Zhao, J. Zhang, X. Zhu, M. Zhang, J. Tang, M. Tan, Y. Wang, *Appl. Catal., B.* **2014**, *144*, 468-477.
- [3] J. Lv, T. Kako, Z. Li, Z. Zou, J. Ye, *J. Phys. Chem. C.* **2010**, *114*, 6157-6162.