

Supporting information

Coordination environment dominated catalytic selectivity of photocatalytic hydrogen and oxygen reduction over switchable gallium and nitrogen active sites

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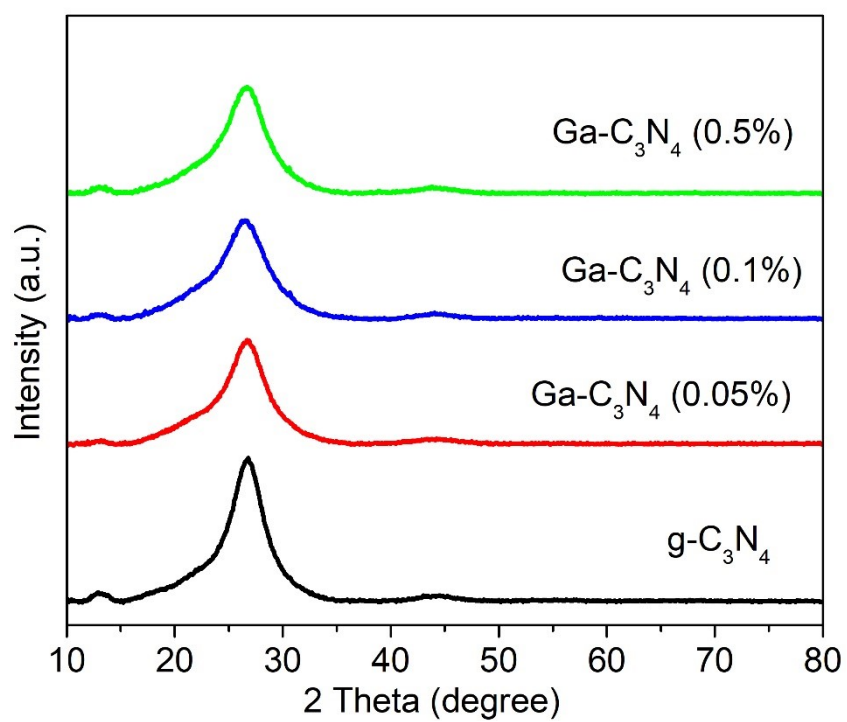


Figure S1. XRD patterns of pure C₃N₄ and Ga-coordinated C₃N₄ samples.

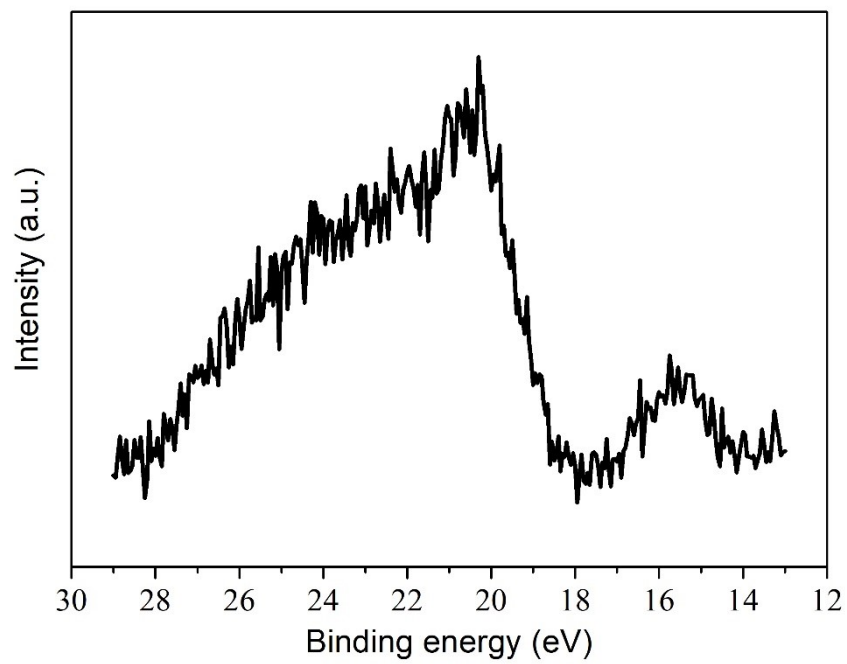


Figure S2. High-resolution XPS of Ga_{3d} in the Ga-C₃N₄ sample.

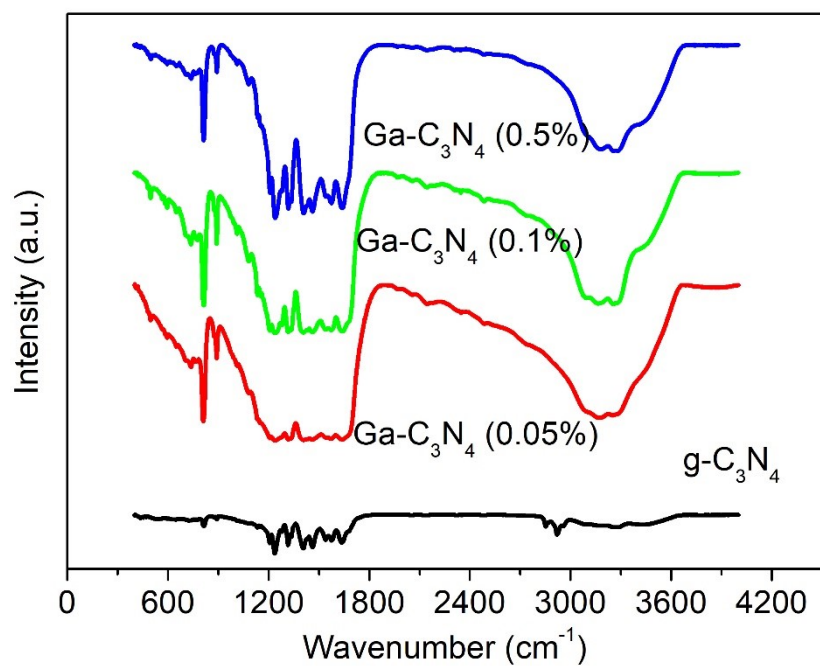


Figure S3. FTIR spectra of pure C₃N₄ and Ga-coordinated C₃N₄ samples.

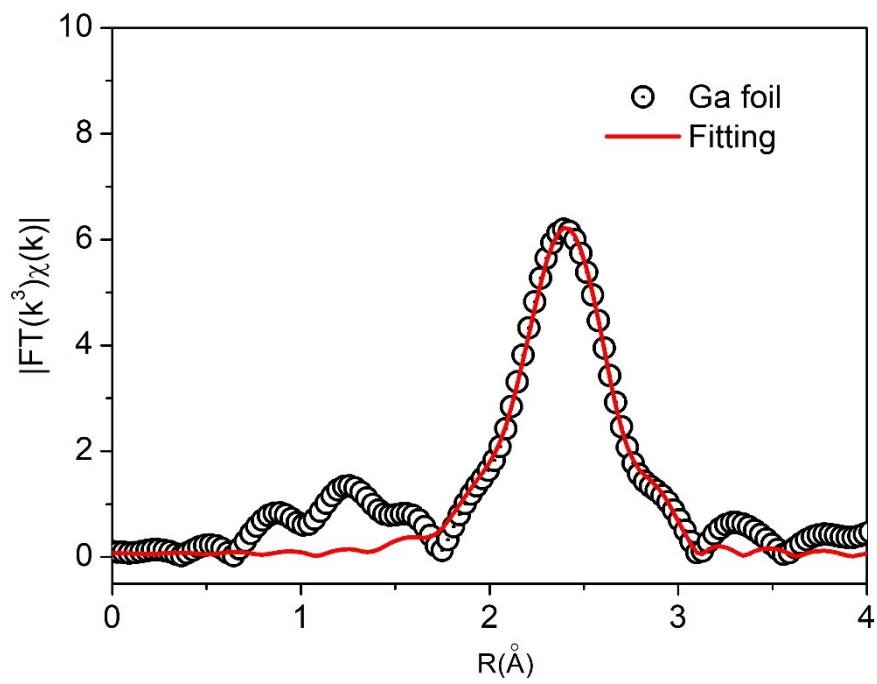


Figure S4. Fitted FT-EXAFS curve at R space for Ga foil.

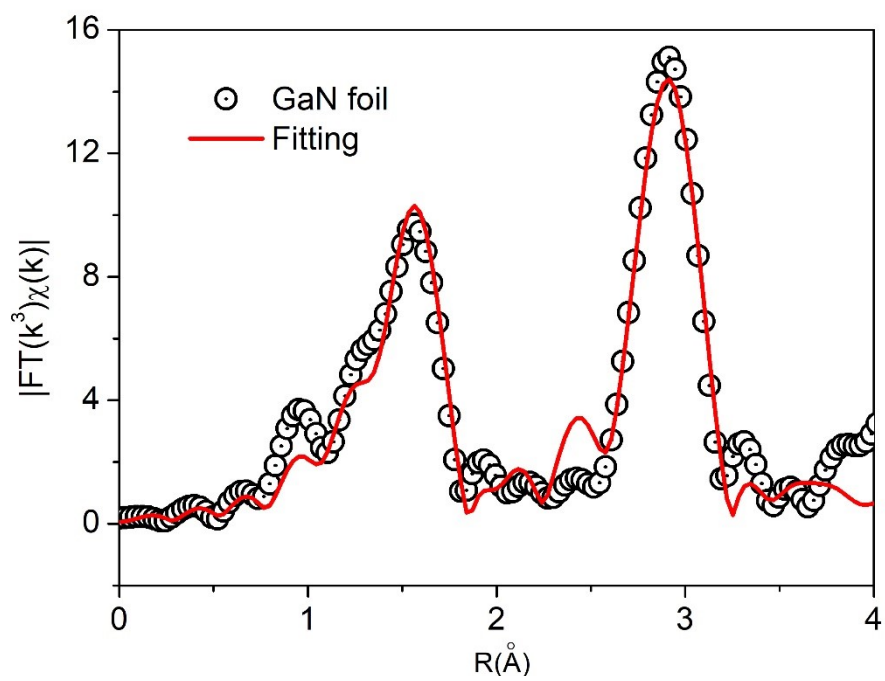


Figure S5. Fitted FT-EXAFS curve at R space for GaN reference.

Table S1. Fitting parameters of Ga K-edge EXAFS of Ga-doped g-C₃N₄ nanosheets and reference samples.

Sample	Shell	CN	R (Å)	$\sigma^2(\text{Å}^2)$	ΔE^0 (eV)	S_0^2
Ga_1	Ga-N	3.9	1.95	0.010	3.3	0.99
Ga_2	Ga-N	5.0	1.95	0.009	3.3	0.99
Ga_3	Ga-N	5.9	1.95	0.010	3.8	0.99
Ga foil	Ga-Ga1	1	2.60	0.006	6.3	0.99
	Ga-Ga2	2	2.72	0.005	6.3	0.99
	Ga-Ga3	2	2.82	0.011	6.3	0.99
	Ga-Ga4	2	2.83	0.011	6.3	0.99
GaN	Ga-N	4	1.95	0.004	3.9	0.99
	Ga-Ga	12	3.22	0.012	3.9	0.99

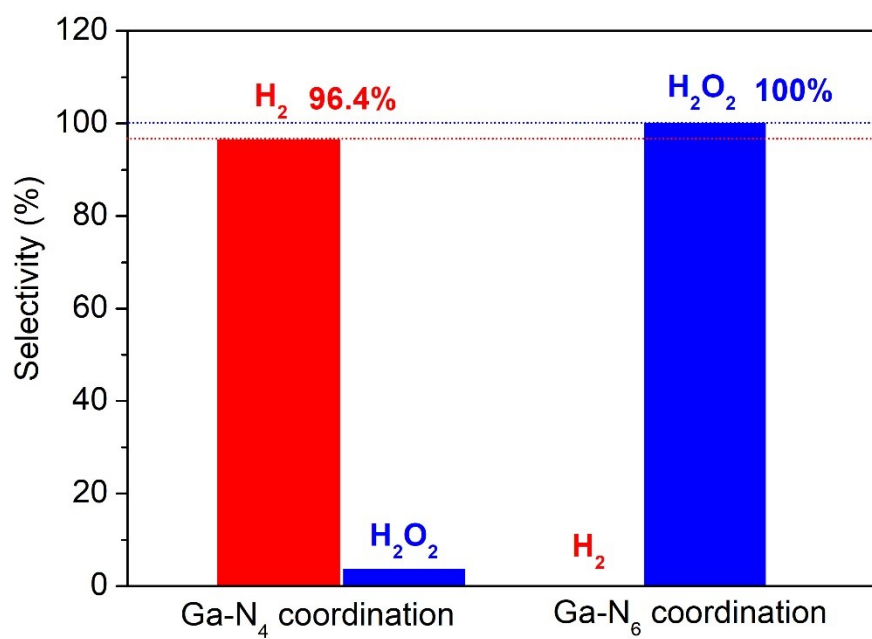


Figure S6. Photocatalytic selectivity of Ga-N₄ and Ga-N₆ coordinated C₃N₄ samples.

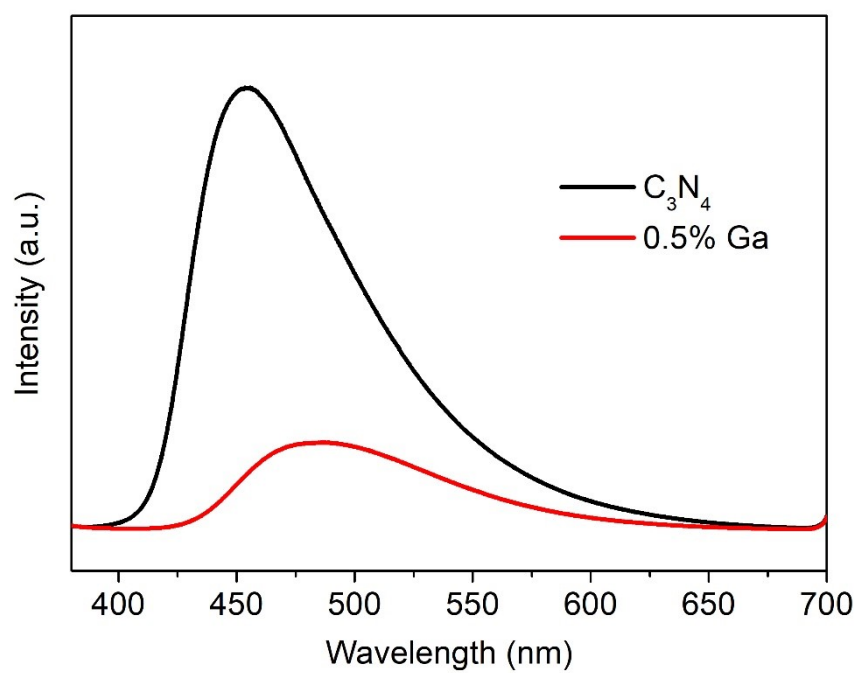


Figure S7. PL spectra of pure C_3N_4 and Ga-coordinated C_3N_4 samples.

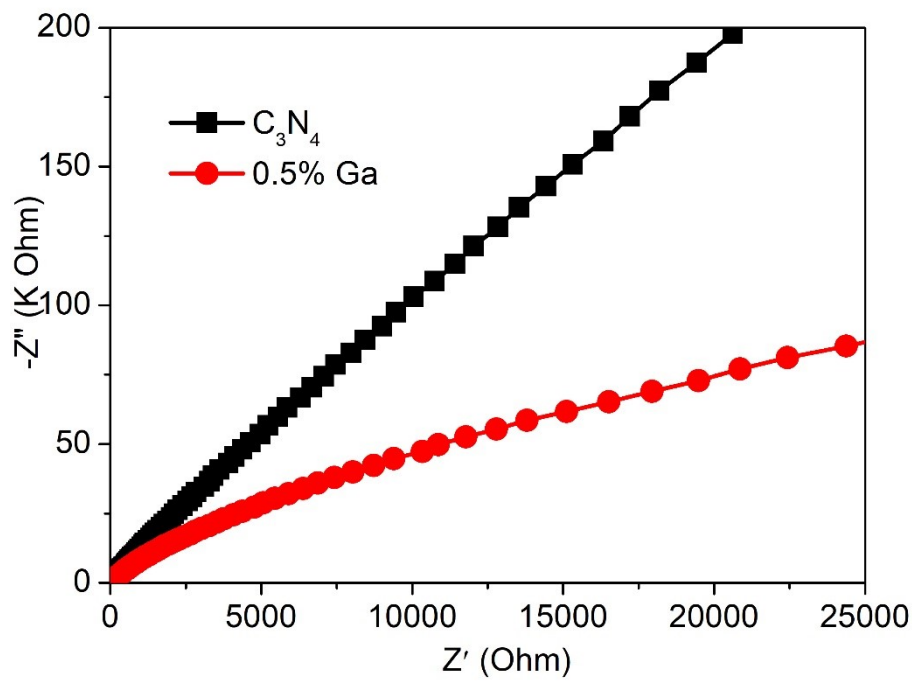


Figure S8. EIS spectra of pure C_3N_4 and Ga-coordinated C_3N_4 samples.

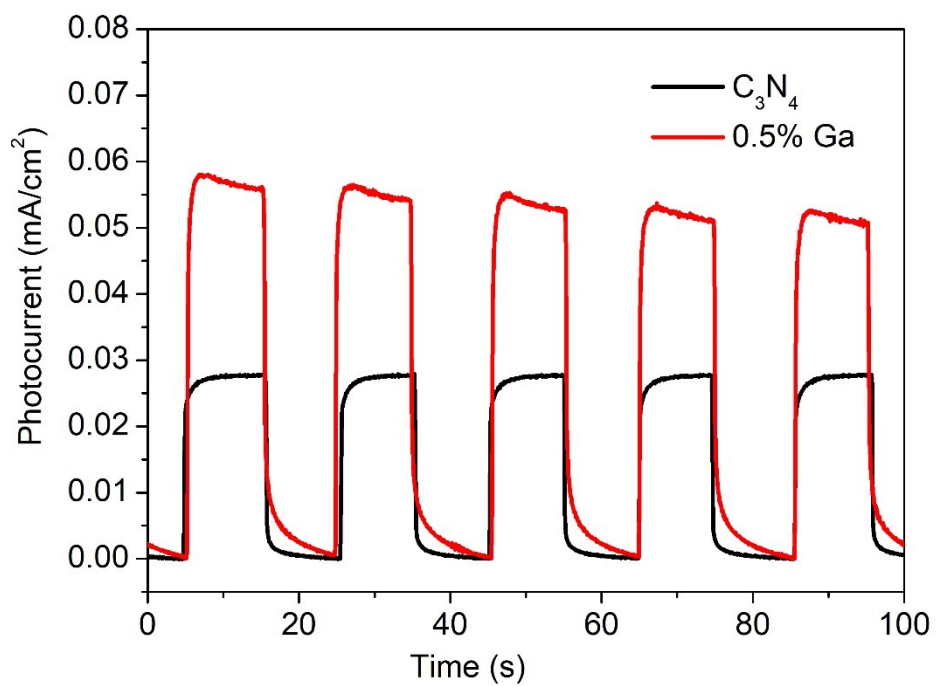


Figure S9. Transient photocurrent curves of pure C₃N₄ and Ga-coordinated C₃N₄ samples.

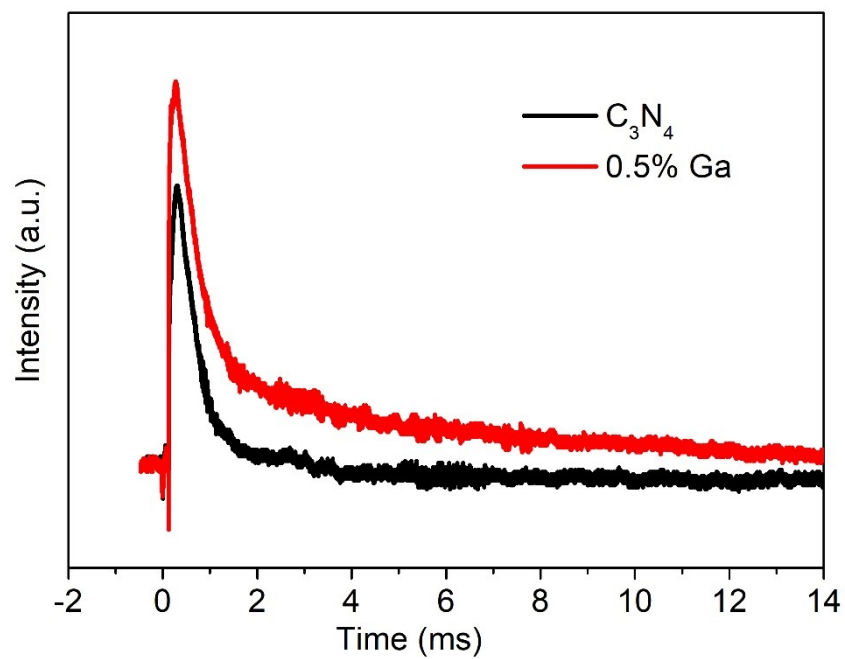


Figure S10. TPV spectra of pure C_3N_4 and Ga-coordinated C_3N_4 samples.

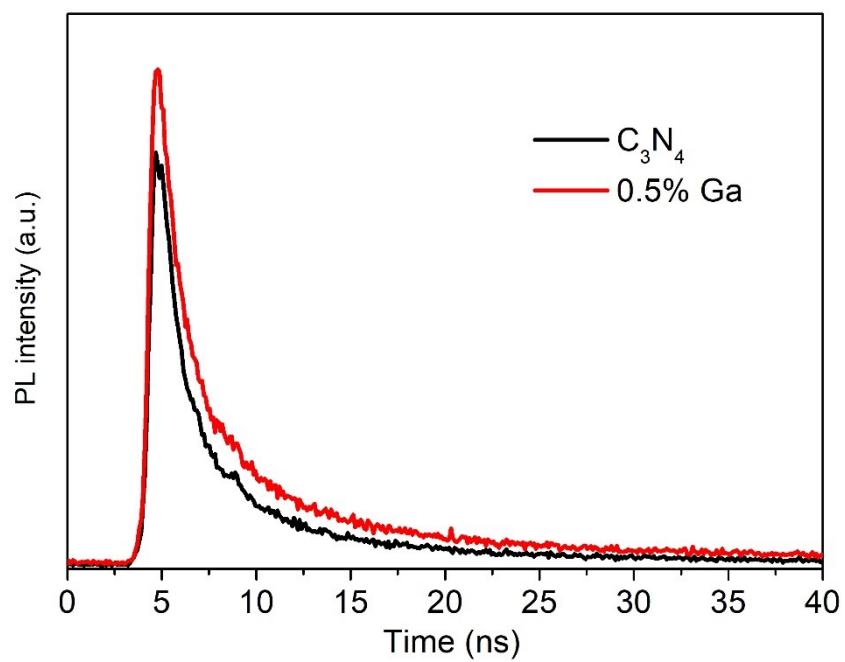


Figure S11. Time-resolved PL spectra of pure C_3N_4 and Ga-coordinated C_3N_4 samples.

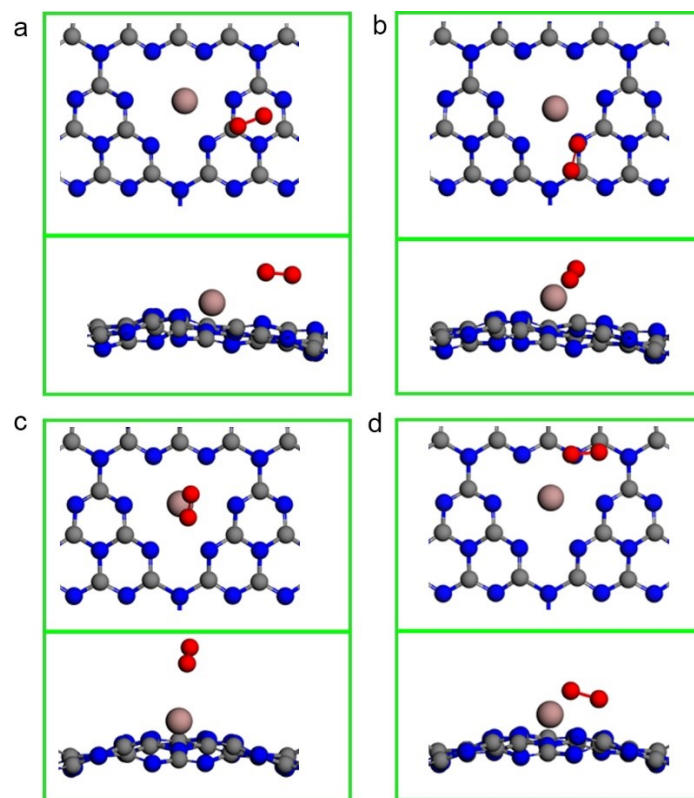


Figure S12. (a) O_2 adsorption on C sites (0.822 eV). (b) O_2 adsorption on N sites (0.522 eV). (c) O_2 adsorption on Ga sites (0.898 eV). (d) O_2 adsorption on N sites (0.556 eV).

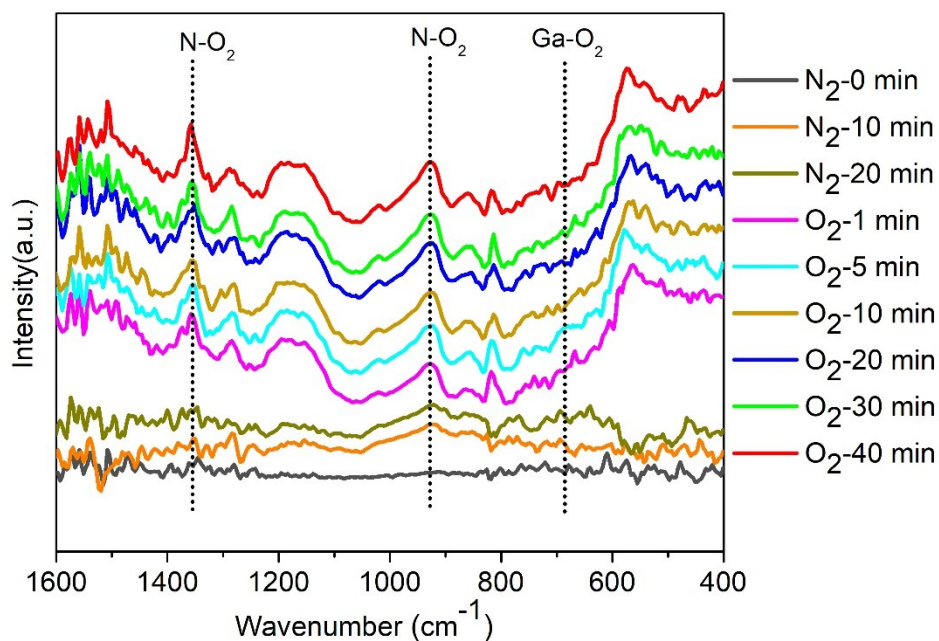


Figure S13. In-situ diffuse reflectance infrared transform spectra of the Ga-N₆ coordinated sample under N₂ and O₂/H₂O condition.

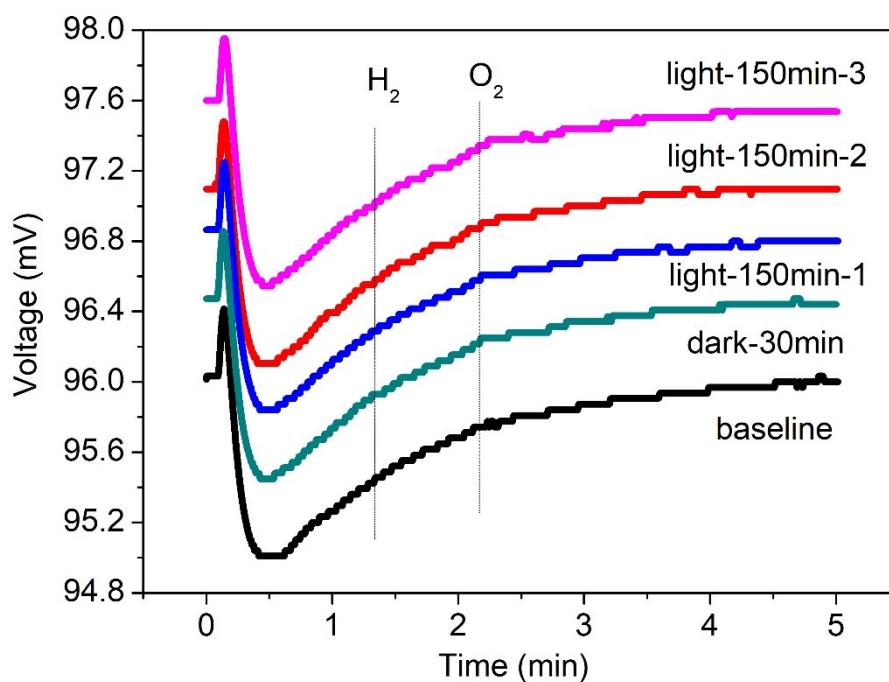


Figure S14. Detection of H₂/O₂ signals by GC-TCD. The baseline curve was shown for reference. The gas in the reactor was kept for 30 min under dark condition to realize the adsorption-desorption equilibrium, and then was detected by GC-TCD. Light-150min-1/2/3 denotes that the photocatalytic process was performed under light irradiation for 150 min, and then the gas in the reactor was collected and examined by GC-TCD for three times.

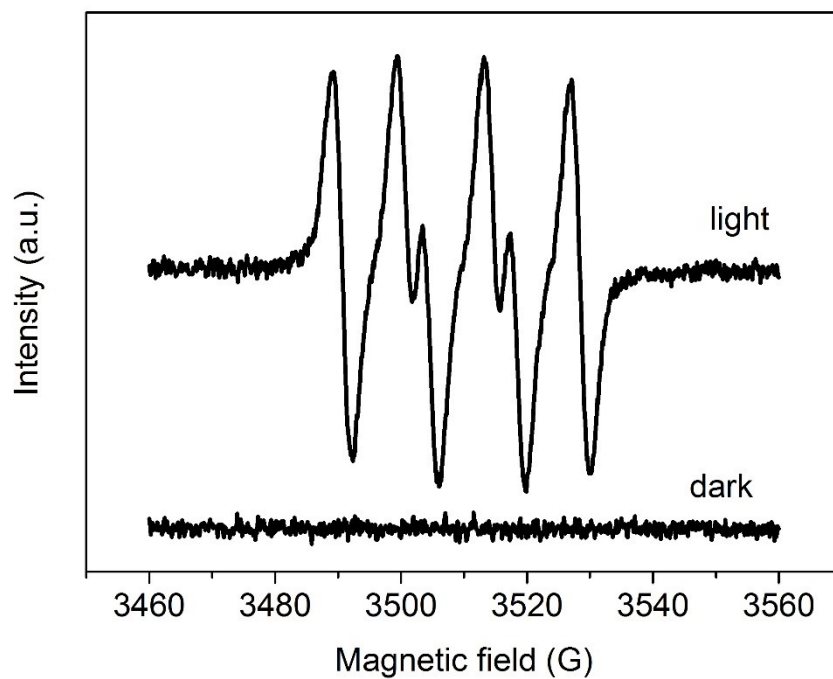


Figure S15. Superoxide radicals under dark condition and under light irradiation.

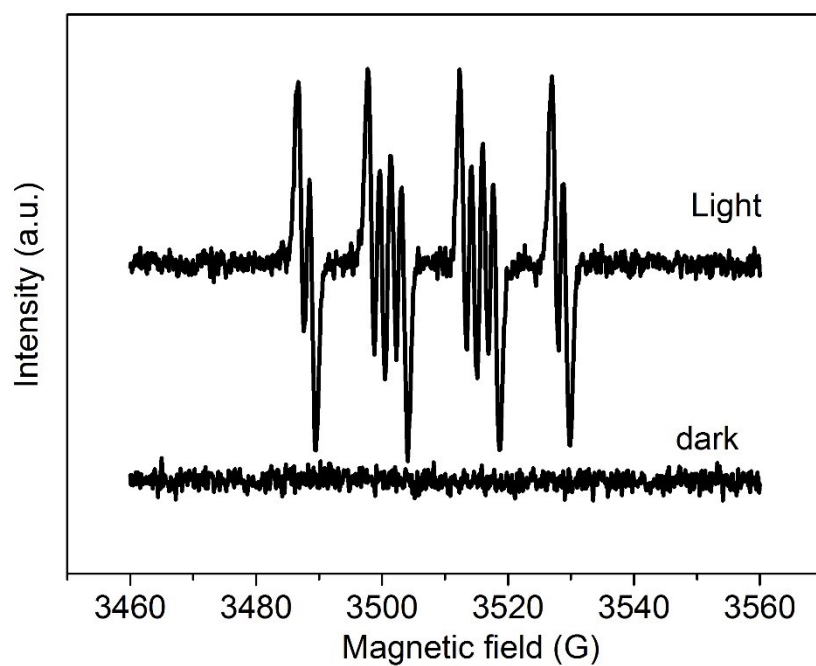


Figure S16. \bullet OOH radicals under dark condition and under light irradiation.

