Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

One-step Green Conversion of Benzyl Bromide to Aldehydes on NaOH-modified g-C_3N_4 with Dioxygen under LED Visible Light

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S1. Synthesis of g-C_3N_4-HV and Na/ g-C_3N_4-HV

g-C_3N_4-HV was prepared followed the method reported previously, which under the further alkali treatment with NaOH to obtain the sample Na/g-C_3N_4-HV. In a typical synthesis procedure, cyanimide (5 g) was loaded in a porcelain boat and then treated in a pipe furnace at 500 °C for 4 h under flowing nitrogen (60 $mL \cdot min^{-1}$) with a ramp rate of 1 $°C \cdot min^{-1}$. For the preparation of g-C_3N_4-HV, the resulting light yellow powder (g-C_3N_4) was sequentially treated in vacuum (10^{-2} Torr) at 550 °C for 1h. The NaOH treated g-C_3N_4-HV sample (Na/g-C_3N_4-HV) was synthesized by impregnation method. The g-C_3N_4-HV was added in NaOH solution (5 wt.%) with continuously agitation at 200 °C until the complete evaporation of water. The resulting powder was washed several times with deionized water and then dried in air oven at 60 °C.

S2. Reactor Ventilation O_2 Steps

The operation of introducing O_2 was carried out in a double row tube. O_2 was introduced into the reaction tube by inserting a steel needle (20 cm) connecting an oxygen source with a rubber tubing to the bottom of the tube. Four Schlenk tubes with photocatalyst, solvent and substrate was bubbled by O_2 at the same time. The total flow rate was 20 mL/min and 5 mL/min each. The reactor was continuously exhausted with flow rate 20 mL/min of O_2 for 30 min and then was kept in O_2.

S3. Correlation calculation

Theoretically, the nitrogen atoms mainly have two chemical states in the triazine-based carbon nitride, including 75% (N1) in C_3N_3 rings and 25% (N2) serving as bridge groups. In the tri-s-triazine-based carbon nitride, there are three main types of N species, including 75% N1 (idem), 12.5% N2 (idem), and 12.5% N3 (N in the center of the tri-s-triazine ring) [1]. N1 is the sp^2-hybridized aromatic N bonded to carbon atoms (C≡N-C), involving two σ bonds and one π bond. N2 and N3 have three σ bonds, but N3 is located within tri-s- triazine and shared by three triazine rings. The lone pairs electrons of N3 are conjugated with the π electron of three rings [2]. It is estimated accordingly that N3 atoms have more positive charge than N1 and N2 atoms and thus higher bonding energy than N1 and N2 [3].

C_H=N3/12.5%, C_H: Heptazine rings content (%)

Bridge sites content (%) = (100-C_H)×25%+C_H×12.5%

S4. Characterization and selective oxidation activity of g-C_3N_4-HV and Na/g-C_3N_4-HV.

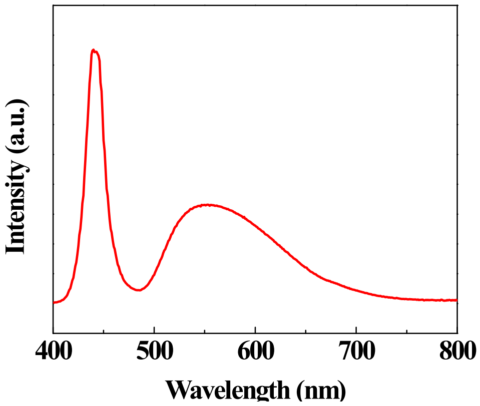

Figure S1. The spectrogram of the LED lamp

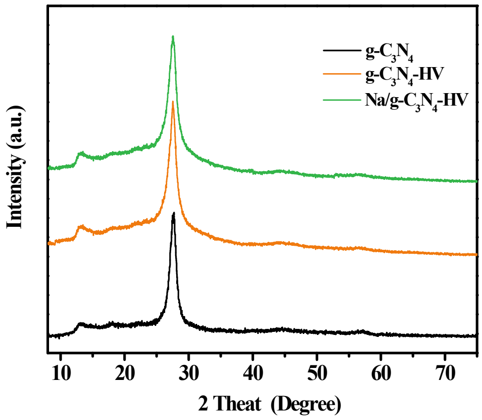

Figure S2. XRD pattern of g-C_3N_4, g-C_3N_4-HV and Na/g-C_3N_4-HV sample.

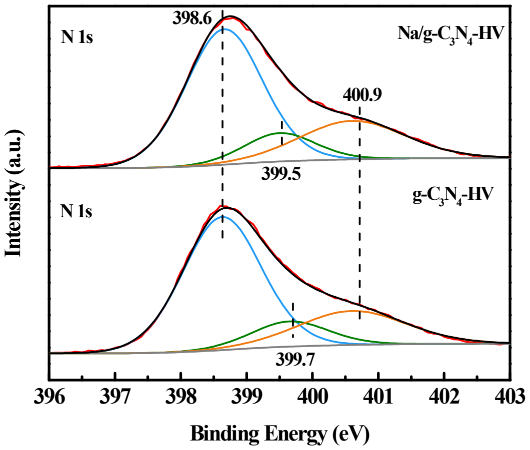

Figure S3. N 1s high-resolution XPS spectra for g-C_3N_4-HV and Na/g-C_3N_4-HV sample.

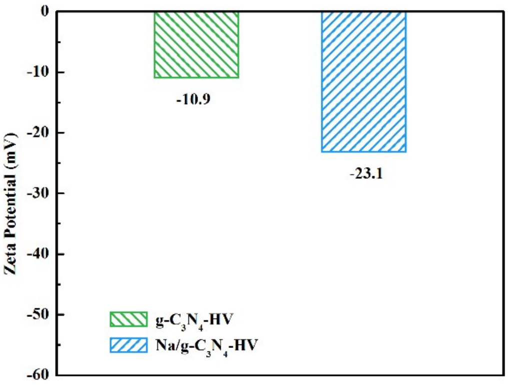

Figure S4. Zeta potential of g-C_3N_4-HV and Na/g-C_3N_4-HV sample measured in H_2O (pH=7).

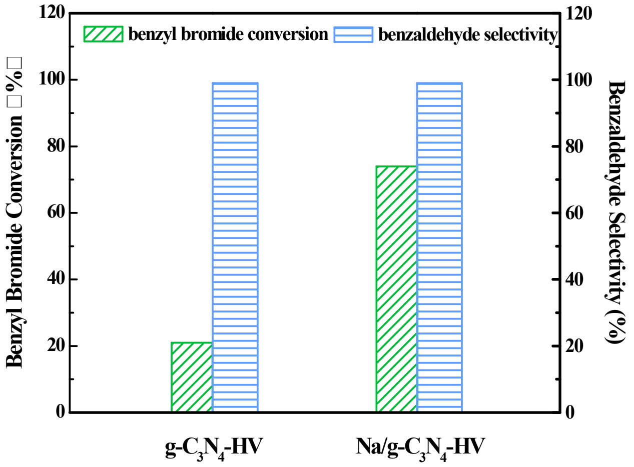

Figure S5. Photocatalytic performance of g-C_3N_4-HV and Na/g-C_3N_4-HV for the oxidation of benzyl bromide with O_2.

Table S1. Distribution of N atoms in g-C_3N_4, g-C_3N_4-HV, Na/g-C_3N_4-HV.

	Sample	N1	N2	N3	Bridge sites content (%)*
	B.E (eV)	398.7±0.1	399.7±0.3	401.0±0.1	
Atom content (%)	g-C_3N_4	72.20	20.58	7.22	17.78
	g-C_3N_4-HV	72.53	16.56	10.91	14.09
	Na/g-C_3N_4-HV	72.46	16.68	10.86	14.14

* Bridge sites content (%) = (100-N3/12.5%)×25%+N3/12.5%×12.5%

References

[1] Y. Sun, C. Li, Y. Xu, H. Bai, Z. Yao and G. Shi, Chem. Commun., 2010, 46, 4740.

[2] Q. Guo, Q. Yang, L. Zhu, C. Yi, S. Zhang and Y. Xie, Solid State Commun., 2004, 132, 369.

[3] J. Liu, T. Zhang, Z. Wang, G. Dawson and W. Chen, J. Mater. Chem., 2011, 21, 14398.