

Supporting Information for

Is C₃N₄ Chemically Stable towards Reactive Oxygen Species in Sunlight-Driven Water Treatment?

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Number of pages: 18

Number of tables: 2

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Table S1. Elemental composition and estimated chemical formula of NS C₃N₄ and bulk C₃N₄

Sample	C (wt%)	H (wt%)	N (wt%)	Chemical formula	MW (g mol ⁻¹)
NS C ₃ N ₄	34.89	2.28	62.80	C _{2.91} H _{2.28} N _{4.49}	100.06
Bulk C ₃ N ₄	37.10	2.10	60.54	C _{3.09} H _{2.03} N _{4.32}	99.59

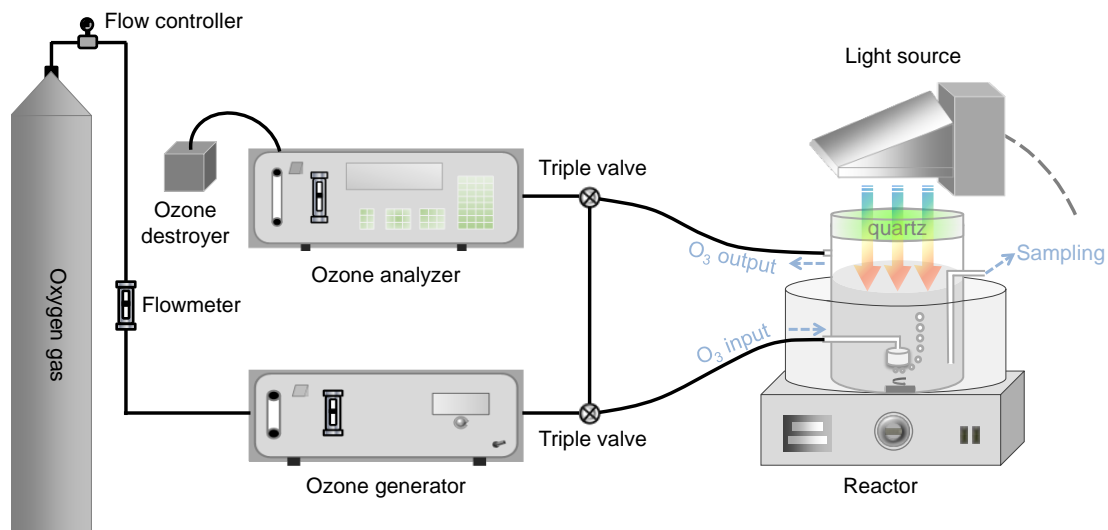


Figure S1. Experimental set-up of photocatalytic ozonation.

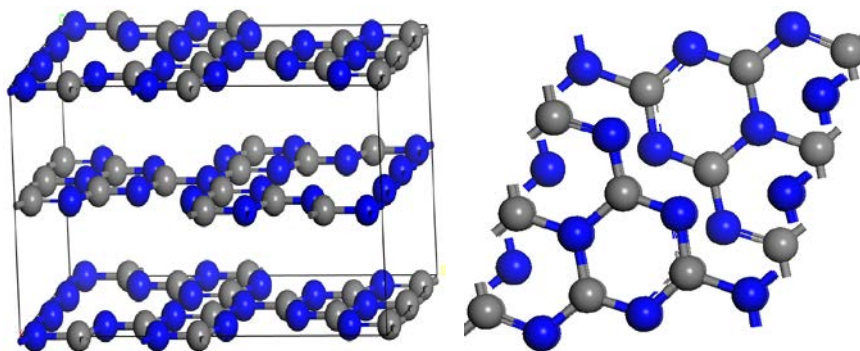


Figure S2. Unit-cell structure of hexagonal heptazine-based C_3N_4 .

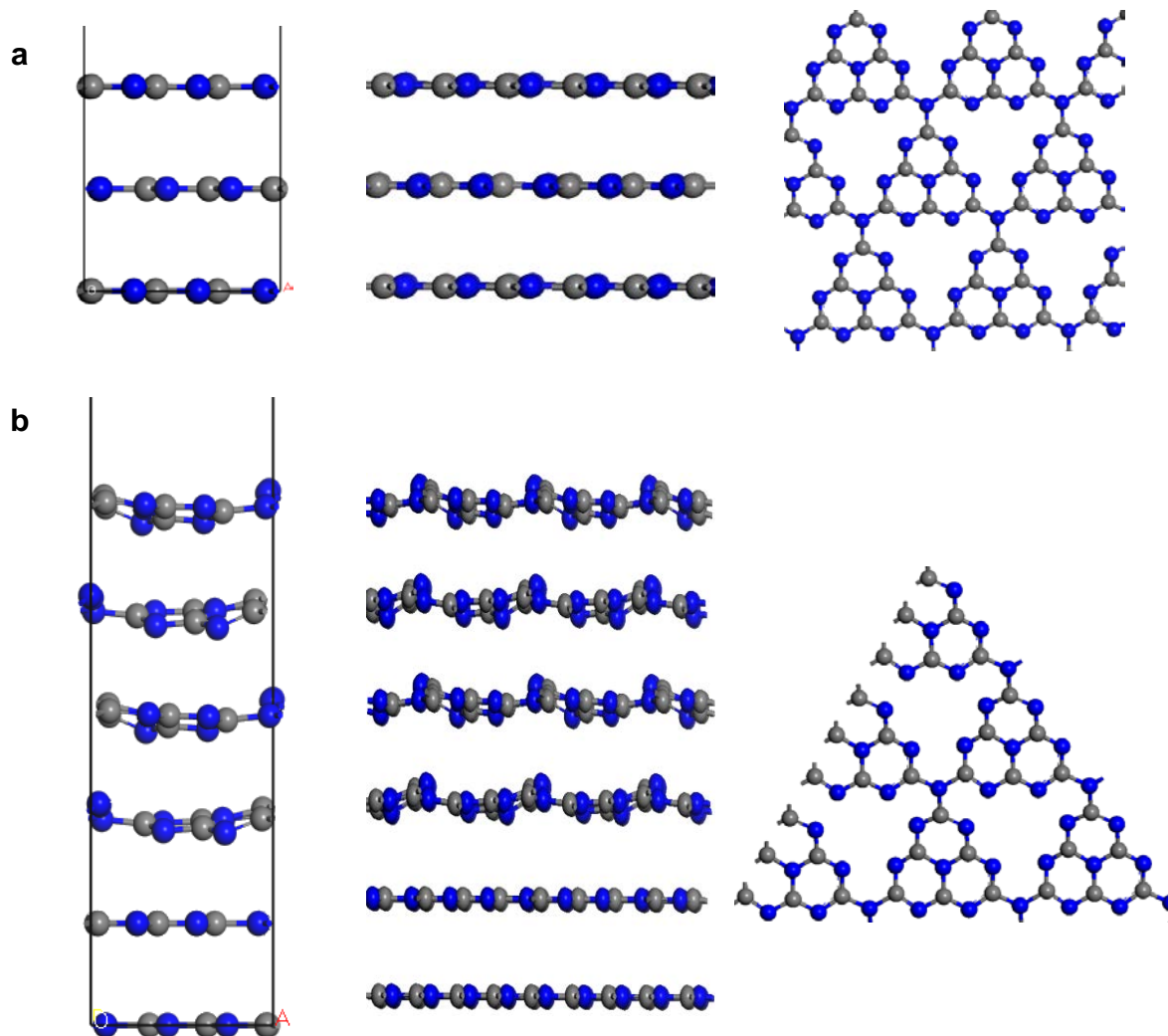


Figure S3. Surface structure of (a) three- and (b) six-layer C_3N_4 . All the atoms in the same layer remain coplanar for 3-layer C_3N_4 , while for 6-layer C_3N_4 , the atoms in the same layer except the two fixed bottom layers are not coplanar due to the relaxation effect. The relaxation effect is the most obvious on the top surface layer due to the strong van der Waals force between layers.

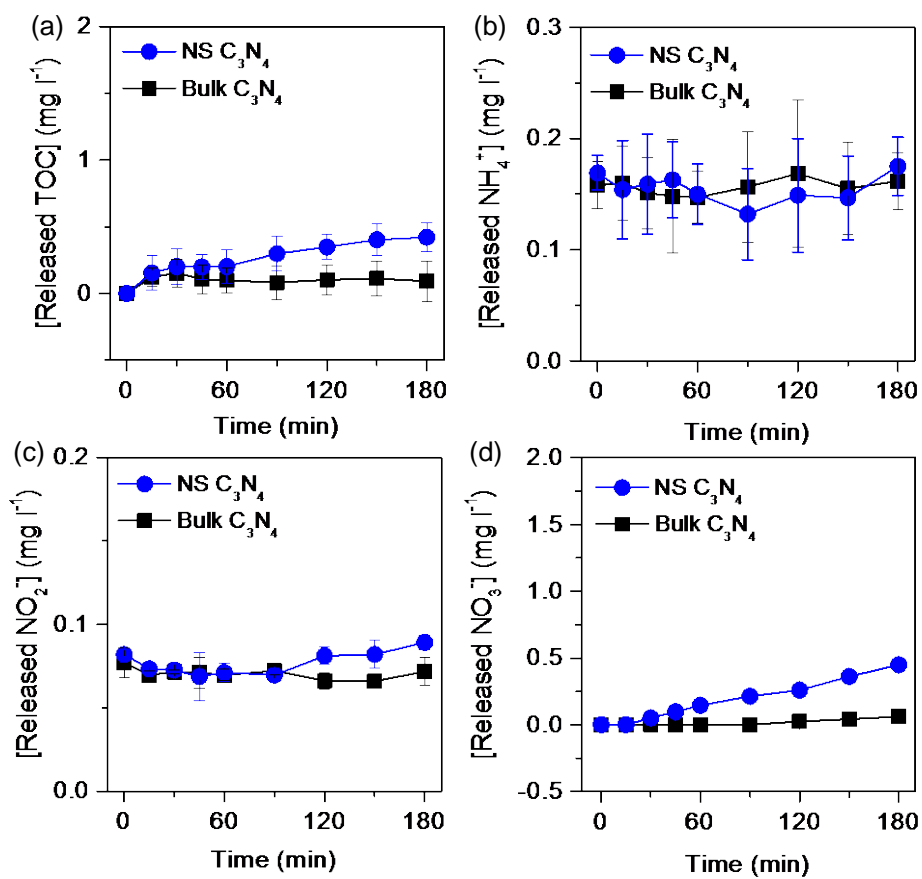


Figure S4. The concentration of (a) TOC, (b) NH_4^+ , (c) NO_2^- and (d) NO_3^- detected in aqueous solution as a function of time during photocatalytic oxidation (sunlight/ $\text{O}_2/\text{C}_3\text{N}_4$). Data reported are an average of three independent experiments.

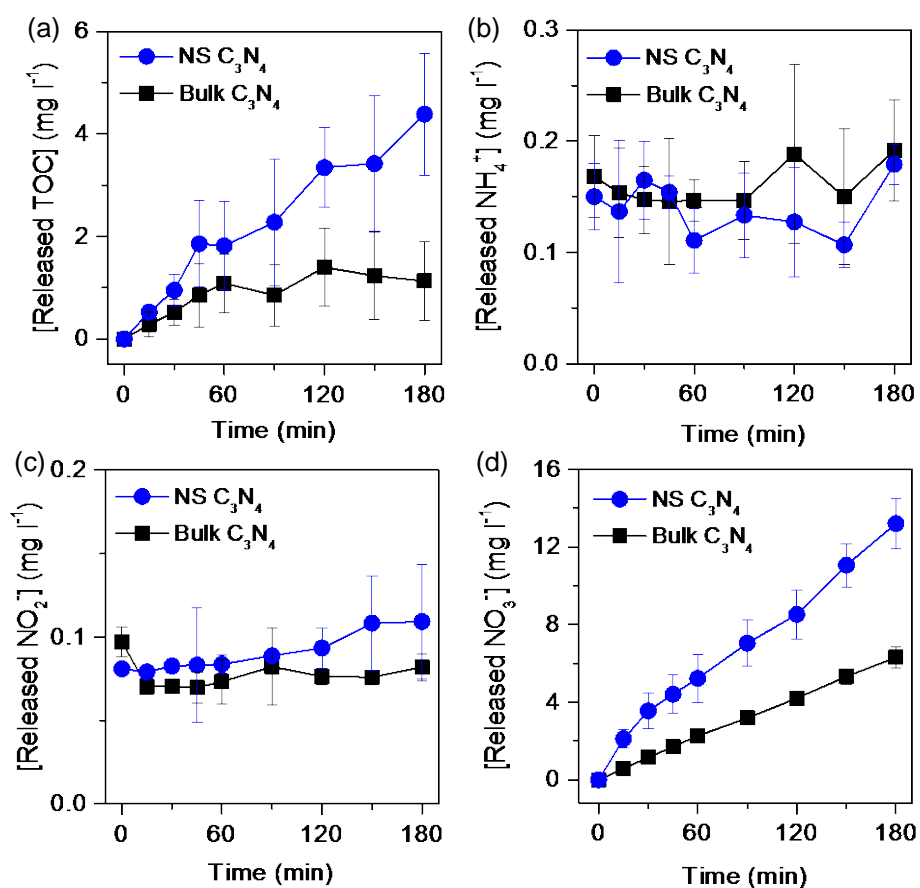


Figure S5. The concentration of (a) TOC, (b) NH_4^+ , (c) NO_2^- and (d) NO_3^- detected in aqueous solution as a function of time during photocatalytic ozonation (sunlight/ $\text{O}_3/\text{C}_3\text{N}_4$). Data reported are an average of three independent experiments.

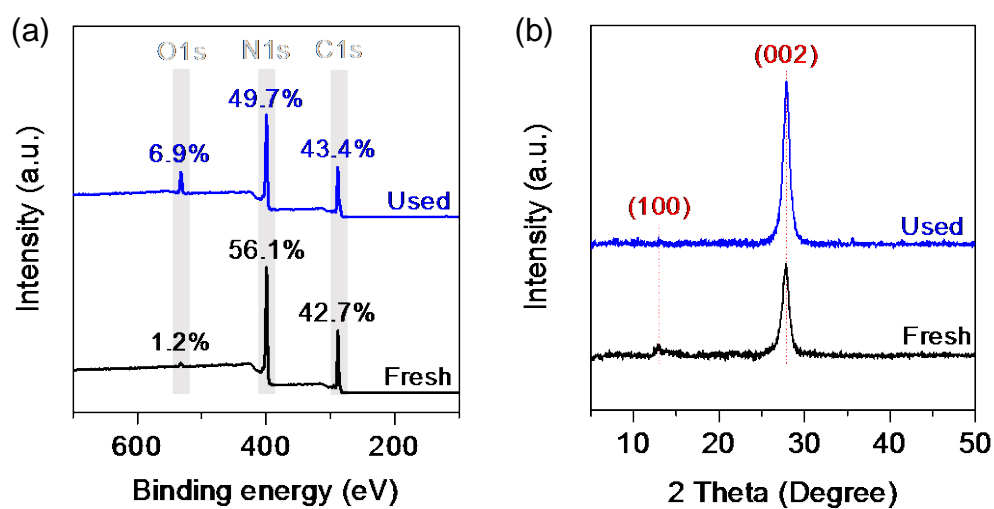


Figure S6. (a) XPS survey spectra and (b) XRD patterns of NS C_3N_4 before and after photocatalytic ozonation for 10 h. Note: The used NS C_3N_4 was collected and naturally dried under ambient conditions.

Table S2. Surface energy of three and six-layer C₃N₄

Layer number	N	A (10 ⁻²⁰ m ²)	E _{slab} (10 ⁻¹⁹ kJ)	E _{bulk} (10 ⁻¹⁹ kJ)	E _{surf} (10 ⁻⁴ kJ m ⁻²)
3	6	44.0984	-14.8753	-2.47952	2.06357
6	12	44.0984	-29.7544	-2.47952	-0.18141

The surface energy of 6-layer C₃N₄ (-0.18141×10^{-4} kJ m⁻²) was significantly lower than that of 3-layer one (2.06361×10^{-4} kJ m⁻²), indicating that C₃N₄ with more stacking layers exhibits lower surface energy and thus higher structural stability.

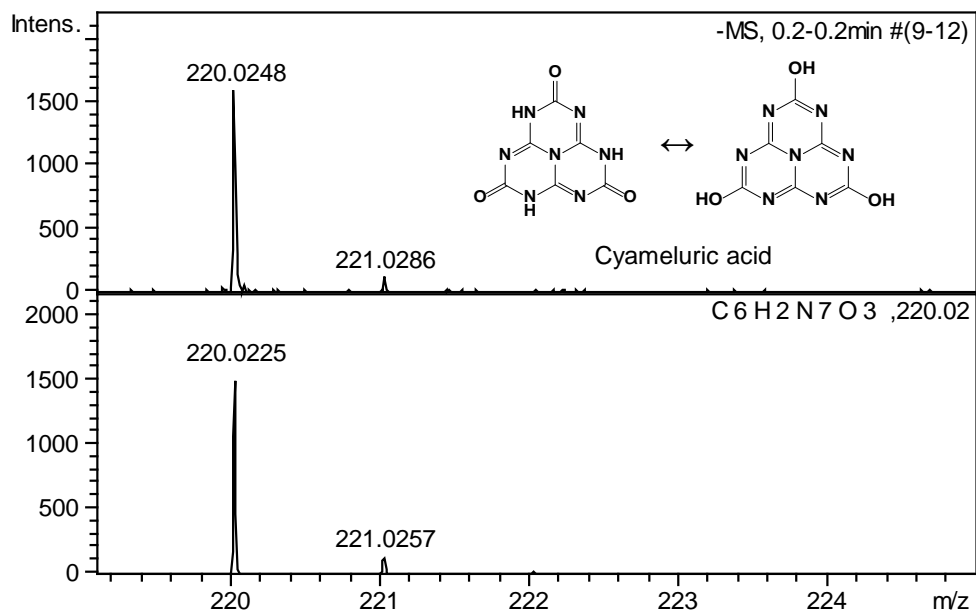


Figure S7. Identification of MS peak at m/z 220.0048 by Compass Isotope Pattern software (Bruker Daltonik). The top is the measured isotope pattern, and the bottom is the theoretically predicted one.

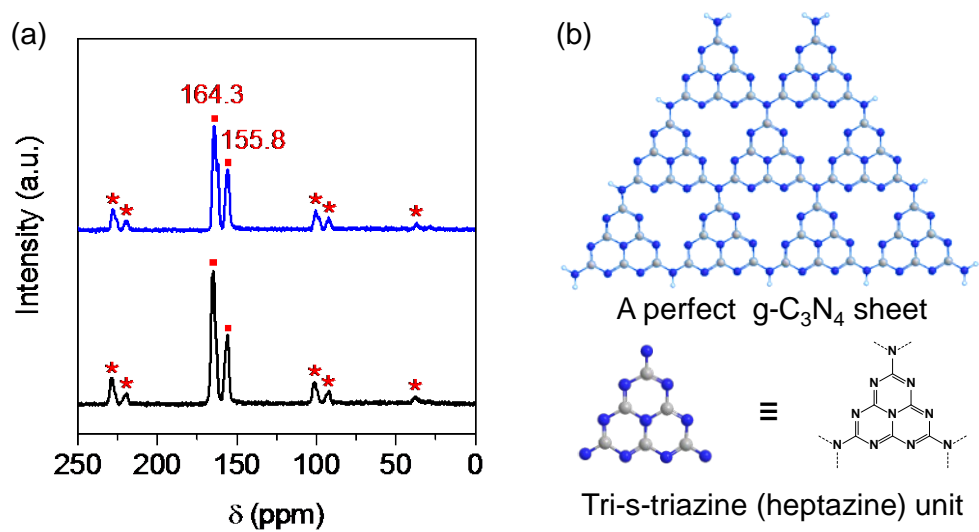


Figure S8. (a) Solid-state ^{13}C NMR spectra of NS C_3N_4 and bulk C_3N_4 . *Indicates the spinning side bands in the ^{13}C spectra. (b) Illustration of a perfect molecular C_3N_4 structure composed of tri-s-triazine (heptazine) units.

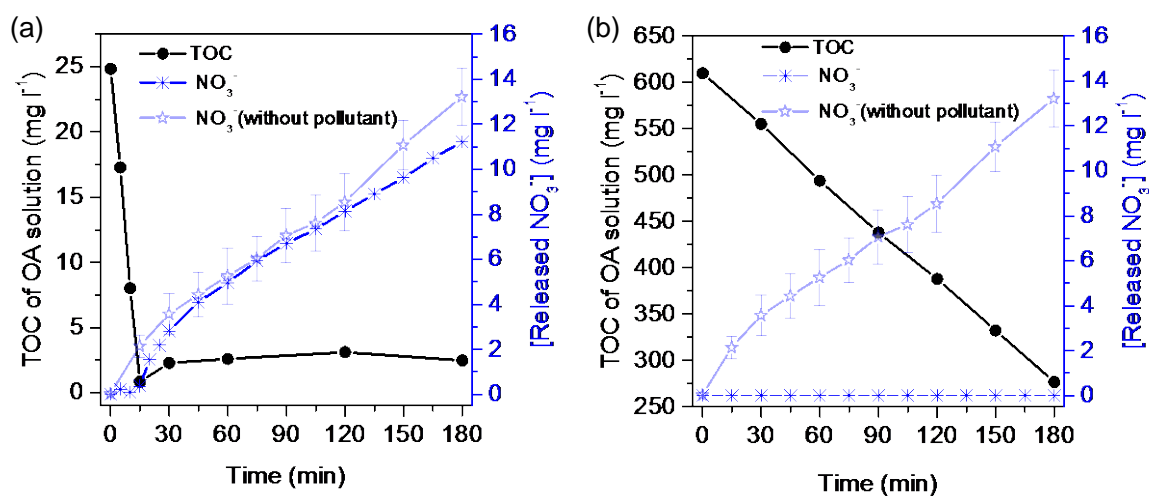


Figure S9. Concentrations of TOC and NO₃⁻ in solution as a function of time during sunlight/O₃/NS C₃N₄ treatment of (a) 1 mM OA and (b) 25 mM OA. The five-pointed star indicates the concentration of NO₃⁻ in initially ultrapure water during sunlight/O₃/NS C₃N₄ process.

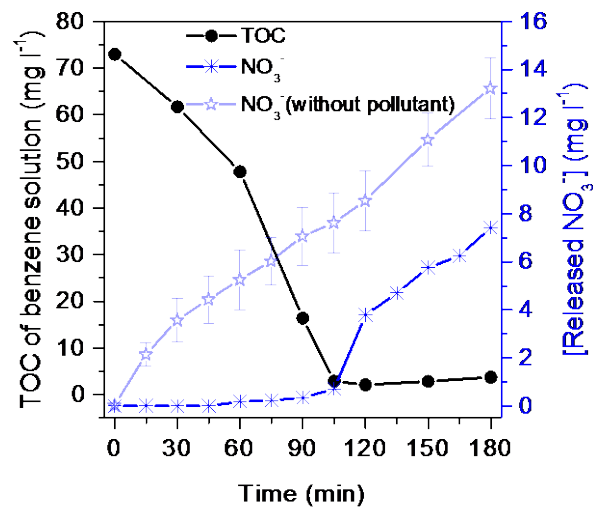


Figure S10. Concentrations of TOC and NO_3^- in solution as a function of time during sunlight/ O_3 /NS C_3N_4 treatment of 1 mM benzene. The five-pointed star indicates the concentration of NO_3^- in initially ultrapure water during sunlight/ O_3 /NS C_3N_4 process.

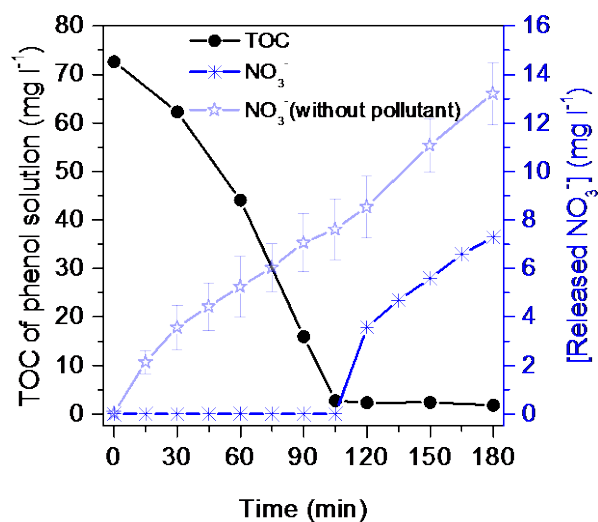


Figure S11. Concentrations of TOC and NO_3^- in solution as a function of time during sunlight/ O_3 /NS C_3N_4 treatment of 1 mM phenol. The five-pointed star indicates the concentration of NO_3^- in initially ultrapure water during sunlight/ O_3 /NS C_3N_4 process.

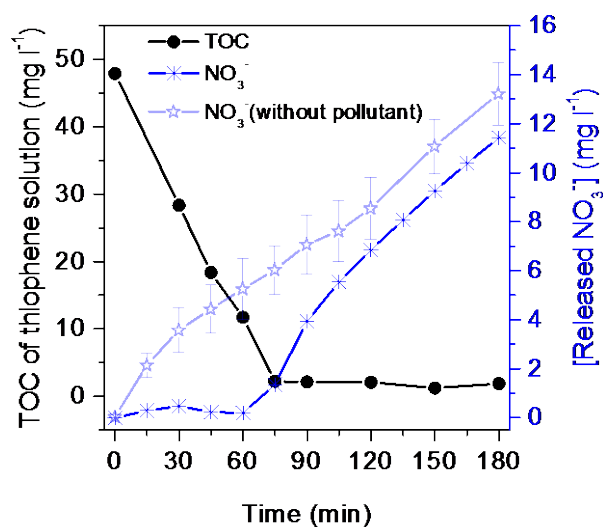


Figure S12. Concentrations of TOC and NO_3^- in solution as a function of time during sunlight/ O_3 /NS C_3N_4 treatment of 1 mM thiophene. The five-pointed star indicates the concentration of NO_3^- in initially ultrapure water during sunlight/ O_3 /NS C_3N_4 process.

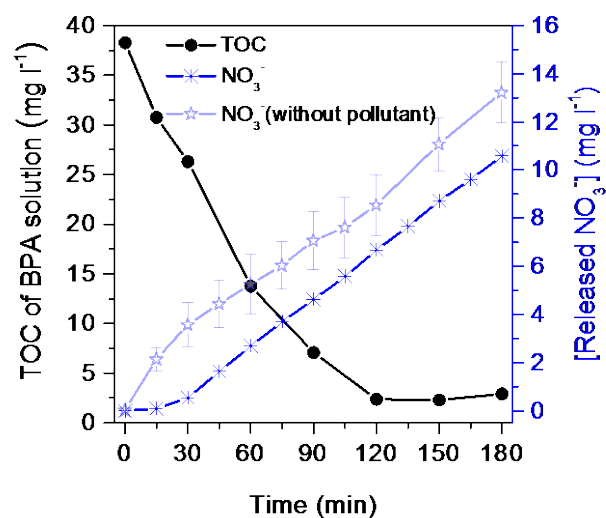


Figure S13. Concentrations of TOC and NO₃⁻ in solution as a function of time during sunlight/O₃/NS C₃N₄ treatment of 0.22 mM (50 mg l⁻¹) BPA. The five-pointed star indicates the concentration of NO₃⁻ in initially ultrapure water during sunlight/O₃/NS C₃N₄ process.

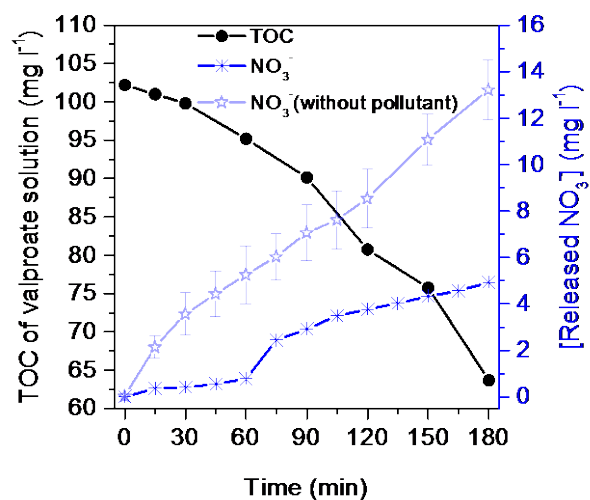


Figure S14. Concentrations of TOC and NO₃⁻ in solution as a function of time during sunlight/O₃/NS C₃N₄ treatment of 1 mM valproate. The five-pointed star indicates the concentration of NO₃⁻ in initially ultrapure water during sunlight/O₃/NS C₃N₄ process.

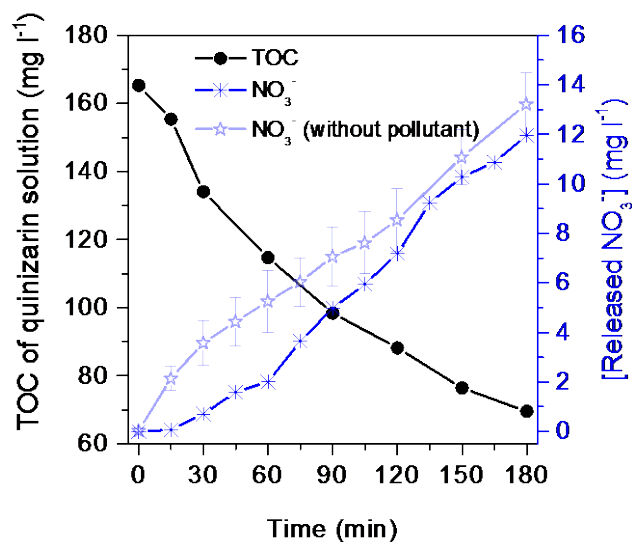


Figure S15. Concentrations of TOC and NO₃⁻ in solution as a function of time during sunlight/O₃/NS C₃N₄ treatment of 1 mM quinizarin. The five-pointed star indicates the concentration of NO₃⁻ in initially ultrapure water during sunlight/O₃/NS C₃N₄ process.