Supporting information for

Structural distortion in graphitic-C₃N₄ realizing efficient photoreactivity

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S1. Experimental Section

Preparation of pristine g- C_3N_4 : The pristine g- C_3N_4 was prepared by polymerization of melamine molecules under high temperature. In detail, melamine was put into a crucible with a cover and heated at 600 °C for 2 h in a muffle furnace with a ramp rate of about 3 °C/min for both the heating and cooling processes. The obtained yellow product was the pristine g- C_3N_4 powder.

*Preparation of F-doped g-C*₃ N_4 : F-doped g-C₃ N_4 was prepared by by directly heating the mixture of 5 g melamine and 0.2 g potassium fluoride at 600 °C for 2 h in a muffle furnace with a ramp rate of about 3 °C per minute for both the heating and cooling processes.

Preparation of F-doped g-C₃N₄ with structural distortion: In this manuscript, the structural distortion of as-obtained product was introduced by F-doping and further heat treatment. In a typical procedure (Scheme 1), 0.5 g of the as-prepared pristine g-C₃N₄ and 0.2 g Potassium fluoride (KF) was mixed together, and then heated at a relatively low temperature of 400 °C for different times, during which both of the fluoride and structural distortion were introduced into the crystal of g-C₃N₄ and the obtained yellow-white products were defined as structural distorted F-doped g-C₃N₄. By controlling the time of heating treatment, we prepared a series of F-doped g-C₃N₄ with different degrees of structural distortion, which are F-CN-12, F-CN-24, F-CN-48, F-CN-96 and F-CN-120, respectively. The as-obtained samples were washed with water for several times to remove the excessive KF before use.

Preparation of g**-** C_3N_4 **with structural distortion**: The procedure for the preparation of structural distorted g- C_3N_4 is similar to that of structural distorted F-doped g- C_3N_4 without the presence of fluoride source. In detail, by heating 0.5 g of the as-prepared pristine g- C_3N_4 at 400 °C for different times, a series of g- C_3N_4 with different degrees of structural distortion can be obtained. Herein, we prepared the samples of CN-12, CN-24, CN-48, CN-96 and CN-120 for further study.

Characterizations. The transmission electron microscopy (TEM) images, was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg K α (hv = 1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.6 eV. Room-temperature UV-vis diffuse reflectance spectroscopy (DRS) were recorded on a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer. The Fourier transform infrared (FT-IR) experiment was carried out on a Magna-IR750 FT-IR spectrometer in a KBr pellet, scanning from 4000 to 400 cm⁻¹ at room temperature. X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ = 1.54178 Å). BET nitrogen adsorption–desorption was measured by using a Micromeritics ASAP 2000 system.

Electrochemical test. The Periodic on/off photocurrent response plots were measured on electrochemical station (CHI660B, Shanghai Chenhua Limited, China) in ambient conditions or illuminated under simulated solar light by a 300W Xe lamp (PLS-SXE300/300UV, Trusttech Co., Ltd. Beijing) without filter. The test was performed on a conventional three-electrode cell in 0.5M Na₂SO₄ solution with -0.2V bias vs. Ag/AgCl electrode. In detail, cleaned ITO deposited with a sample film as the working electrode, Pt wire as the counter electrode and standard Ag/AgCl electrode (3M KCl) as the reference electrode, respectively. The carbon nitride electrode was prepared by dropping 20µL aqueous slurry that consisted of 50 mg of prepared sample with 200µL of H₂O, 5µL of acetylacetone, and 5µL of Triton X-100 on a cleaned ITO glass substrate. The sample area was about 1cm². After air dried, the electrode was annealed at 300 °C for 2 h in air. Mott-Schottky tests was performed with the potentials ranged from -0.5V to 1V (vs. Ag/AgCl) at the selected frequencies of 1.2, 1.8 and 2.7 kHz. The electrochemical impedance spectroscopy

(EIS) was carried out in the frequency range of 1 Hz to 10^6 Hz with an AC voltage amplitude of 5 mV.

Photocatalytic test. For photodegradation of organic dyes, 20mg of the catalyst was added into 100mL solution with RhB (6 mg/L) and H₂O₂ (0.5 mL, 30 wt.%), which was ultrasound for about 30 min to make sure the catalyst well dispersed in the solution and further stirred in the dark for 100min to reach the adsorption equilibrium prior to the photocatalytic test. The photocatalytic activity of materials was evaluated by the concentration of RhB remained in solution. Photocatalytic hydrogen evolution was carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass gas system. In detail, 20mg of catalyst powders was dispersed in the aqueous solution (200 mL) containing methanol (20 vol.%) as sacrificial electron donor. Co-catalysts Pt nanoparticles were introduced by in-situ photodeposition method as reported before, where loaded amount of Pt was estimated to be about 3 wt.%. Before test, the reaction solution was evacuated several times to remove air completely prior to irradiation under a 300W Xe-lamp. All the photocatalytic test were performed under full spectrum irradiation of 150 mW/cm². The temperature of the reaction solution was maintained at room temperature by a flow of cooling water during the reaction.

Calculation method. The calculations employed the projected augmented wave method with the Perdew-Burke-Ernzerhof (PBE) GGA functional encoded in the Vienna ab initio simulation package. The energy cut-off was set to 500eV, and the atomic positions are allowed to relax until the energy and force are less than 10^{-5} eV and 0.02 eV/Å, respectively. The Brillouin zones of C₃N₄ slab were sampled in 4×4×1 k-point grids.

S2. Schematic illustration for the design of g-C₃N₄ with structural distortion



Scheme S1. Schematic illustration for the design of $g-C_3N_4$ and F-doped $g-C_3N_4$ with structural distortion, respectively.

S3. Calculation details of F-doped g-C₃N₄



Figure S1. The energy for the different absorption sites of F-doped $g-C_3N_4$, indicating F-atom adsorbed on the C_2 site will be more stable.



Figure S2. Schematic illustration of the structural distortion in F-doped g-C₃N₄.

Considering the electronegativity and coordination number of fluorine, the fluorine cannot occupy the place of carbon or nitrogen atoms in the rigid C-N plane but bond to the carbon or nitrogen. Theoretical simulations show that the fluoride tends to bond with specific carbon atoms for the formation of the most stable molecule (Figure S1). After doping with fluoride, the C-N plane of g-C₃N₄ totally distorts due to the partial conversion of C-sp² to C-sp³ (Figure S2), and structural distortion is simultaneously introduced into the doped structure.



S4. Characterization of samples

Figure S3. Photographs of (a) $g-C_3N_4$ and (b) F-doped $g-C_3N_4$ with different heating time, respectively.



Figure S4. BET surface area and pore-size distribution of as-prepared F-CN-96, CN-96 and pristine g-C₃N₄, respectively.



Figure S5. (a) Survey XPS spectra, (b) F1s spectra, (c) C1s spectra and (d) N1s spectra of the pristine $g-C_3N_4$, CN-96 and F-CN-96, respectively. The F content of the as-prepared F-CN-96 is deduced to be about 0.5 atomic%. The peak around 293 eV in C1s spectra could be assigned to carbon species in the tri-s-triazine ring attached to terminal groups, like the uncondensed -NH₂.^[1] The enhanced intensity and slightly shift of peak of F-CN-96 at 293 eV mainly attributed to the formation of C-F bond and the large electronegativity of F.



Figure S6. (a) EELS spectrum of F-CN-96; (b) Corresponding high-resolution EELS spectrum.



Figure S7. (a) TEM and (b) SEM images of F-CN-96, respectively, indicating its porous structure.



Figure S8. HRTEM image of pristine g-C₃N₄, from which the lattice fringes can be clearly seen.



Figure S9. HRTEM images of $g-C_3N_4$ with different degrees of structural distortion, that are CN-12, CN-48, CN-96, respectively.



Figure S10. HRTEM images of F-doped $g-C_3N_4$ with different degrees of structural distortion, that are CN-12, CN-48, CN-96, respectively.



Figure S11. XRD patterns of (a) distorted $g-C_3N_4$ and (b) distorted F-doped $g-C_3N_4$ with different degrees of structural distortion, respectively. The (002) peaks of as-prepared samples are slightly shift towards high angle with the increase of heat-treat time, indicating the planarizartion of undulated carbon nitride layers during heat-treatment.



Figure S12. (a) Raman spectra of g- C_3N_4 with different degrees of structural distortion. (b) Raman spectra of F-doped g- C_3N_4 with different degrees of structural distortion. (c) Raman spectrum of pristine g- C_3N_4 , which with the relative intensity between D band and G band (I_D/I_G) of about 0.36. (d) The value of I_D/I_G of the samples with different degrees of structural distortion. The Raman spectra were recorded with exciting laser at 325 nm.



Figure S13. (a) and (b) N 1s spectra of $g-C_3N_4$ and F-doped $g-C_3N_4$ with different degrees of distortion. (c) N 1s spectra of pristine $g-C_3N_4$, showing the intensity ratio of N(sp²)/N(sp³) of about 7.36. (d) The intensity ratio of N(sp²)/N(sp³) of the samples with different degrees of structural distortion.

As shown in the Figure S12 above, the Raman spectra were recorded to study the relative intensity between D bands and G bands of the samples with different heating times, which could reflect the structural distortion of the g-C₃N₄. Similar to graphite, the D bands of the g-C₃N₄ located at about 1405 cm⁻¹ is related to structural defects and partially distorted structures of the C-sp², while the G band located at about 1570 cm⁻¹ can be used to explain the degree of graphitization of g-C₃N₄.^[2-4] In that case, the larger value of I_D/I_G is, the more structural distortion of g-C₃N₄ will be.^[2] As can be seen from Figure S12d, the value of I_D/I_G is increased with the increasing of heat treatment time of the samples, that is, the degrees of structural distortion for both of the g-C₃N₄ and F-doped g-C₃N₄ will be increased with the increasing of heat treatment time of 96 h heating treatment.

In order to further validate the structural distortion in the as-prepared samples, the intensity ratio of $N(sp^2)/N(sp^3)$ was studied by XPS analysis. As the quasi-2D structure of the heptazine plane in g-C₃N₄, the $N(sp^2)$ would turn into $N(sp^3)$ when the C-N plane was distorted, and the more of the structural distortion in the as-prepared samples, the more $N(sp^3)$ was. As can be seen from Figure S13, the N1s spectra of the sample can be divided into 3 peaks with core levels at around 398.5, 399.8 and 401.0 eV, which can be attributed to sp^2 -hybridized nitrogen (C–N–C),

sp³-hybridized nitrogen (N–[C]₃) and amino functional groups (C–NH), respectively.^[5] In that case, the larger value of $I_{N(sp2)}/I_{N(sp3)}$ is, the less structural distortion of g-C₃N₄ will be. As shown in the Figure S13d, the pristine g-C₃N₄ possesses the largest value of $I_{N(sp2)}/I_{N(sp3)}$ among the samples of about 7.36. And the value of $I_{N(sp2)}/I_{N(sp3)}$ for the CN-xx and F-CN-xx decreased with increasing of structural distortion, indicating heat treatment and elemental doping can introduce structural distortion into the as-prepared samples. Thus, we believed that based on the HRTEM images, Raman spectra and XPS analysis one could conclude that there was indeed structural distortion in the as-obtained samples.



Figure S14. (a, c) UV-vis absorption spectra of distorted g-C₃N₄ and distorted F-doped g-C₃N₄ with different degrees of structural distortion, respectively. (b, d) The corresponding bandgap estimated by related curves of $(\alpha h \nu)^2 vs$ photon energy plotted.



Figure S15. Mott–Schottky plots of (a) pristine $g-C_3N_4$ and (b) F-CN-96 samples. According to the Mott–Schottky plots, the flat band potentials of F-CN-96 and pristine $g-C_3N_4$ samples were estimated to be -1.24 V and -1.14 V, respectively.



Figure S16. (a) Mott–Schottky plots and (b)valance band (VB) of CN-96. According to the results, the flat band potentials and valence band of CN-96 samples were estimated to be -1.33 V and -1.56 V, respectively.



Figure S17. Comparison of electronic band structure of pristine g-C₃N₄, CN-96 and F-CN-96, respectively.



Figure S18. EIS Nyquist plots for pristine g-C₃N₄, CN-96 and F-CN-96, respectively. As can be seen above, F-CN-96 and CN-96 possessed nearly identical resistances, which were slightly higher than that of pristine g-C₃N₄. This phenomenal can be attribute to the partial conversion from π -bonds to σ -bonds in tri-s-triazine structure of g-C₃N₄, caused by structural distortion. Although the F-CN-96 and CN-96 would exhibit lower charge transfer rates, their charge separation ability are much higher than that of pristine g-C₃N₄, resulting enhanced photocatalytic activity of the modified samples.



Figure S19. (a, b) Periodic on/off photocurrent response of $g-C_3N_4$ and F-doped $g-C_3N_4$ with different degrees of disorder, respectively. (c) Comparison of periodic on/off photocurrent response of pristine $g-C_3N_4$, CN-12, F-CN-12, respectively. Test condition: 0.5 M Na₂SO₄ solution with -0.2 V bias *vs*. Ag/AgCl electrode.



Figure S20. Hydrogen evolution from the mixture of water and methanol with (a) $g-C_3N_4$ and (b) F-doped $g-C_3N_4$ with different degrees of structural distortion under simulated sunlight, respectively. Reaction conditions: 20 mg of catalysts loaded with 3 wt% of Pt; 200 mL of H₂O containing 20 vol% methanol; 300 W Xe lamp.



Figure 21. Hydrogen evolution from the mixture of water and methanol with pristine g-C₃N₄, F-doped g-C₃N₄, CN-96 and F-CN-96 under visible light irradiation (Xe lamp with 420 nm cut-off filters). the hydrogen evolution rates of the F-CN-96 and CN-96 are about 16.7 μ mol·h⁻¹ (i.e. ~835 μ mol·h⁻¹·g⁻¹) and 11.4 μ mol·h⁻¹ (i.e. ~570 μ mol·h⁻¹·g⁻¹) under visible light ($\lambda \ge 420$ nm), which are about 6.2 times and 4.1 times higher than that of the pristine g-C₃N₄ of 2.7 μ mol·h⁻¹, 2.9 times and 2.0 times higher than that of the F-doped g-C₃N₄ of 5.8 μ mol·h⁻¹, respectively. Compared to simulated solar light, the hydrogen evolution rates under visible light decrease significantly, which are manly attributed to the reduced absorption in the visible region, especially for F-CN-96 and CN-96. However, the photocatalytic activities of the F-CN-96 and CN-96 are still much better than that of their pristine counterpart due to their improved charge separation ablity.



Figure 22. Wavelength-dependent apparent quantum yield (AQY) of F-CN-96.



Figure S23. (a) Comparison of photodegradation of RhB with pristine $g-C_3N_4$ and F-CN-96 under simulated sunlight. (b) Cycling tests of photocatalytic degradation of RhB for F-CN-96 under simulated sunlight. (c, d) Photodegradation of RhB with $g-C_3N_4$ and F-doped $g-C_3N_4$ with different degrees of structural distortion under simulated sunlight, respectively. (e) Comparison of time for the photodegradation of 80% RhB for $g-C_3N_4$ and F-doped $g-C_3N_4$ with different degrees of structural distortion. The heat treatment times of the samples are 12 h, 24 h, 48 h, 96 h and 120 h, respectively. Reaction condition: 20 mg of catalysts; 100 mL of RhB solution with concentration of 6 mg/L; 0.5 mL H₂O₂ (30 wt%); 300 W Xe lamp.

Photocatalytic activity of the samples for photodegradation of Rhodamine B (RhB) were carried out to understand the effect of structural distortion on the g-C₃N₄. In a typical procedure for the photodegradation of RhB, 20 mg of the F-CN-96 was added to a 100 mL RhB solution with the concentration of 6 mg/L, and then the above suspension was undergoing an adsorption/desorption equilibrium in dark before illumination. As displayed in Figure S21a, complete photodegradation of RhB only took 5 min for the F-CN-96 under simulated sunlight, while only about 10% of RhB molecules are decomposed for the pristine g-C₃N₄. And the pristine g-C₃N₄ needed up to 50 min for the total degradation of RhB under the same condition as the process for F-CN-96. In addition, the F-CN-96 exhibited negligible reduction of photocatalytic activity under the simulated sunlight after 5 cycles.

The photocatalytic activity of the samples with structural distortion for the photodegradation of RhB is gradually enhanced with increasing degrees of distortion in the structure initially, and then will reaches a balance, and the F-doped g-C₃N₄ with structural distortion shows higher photoactivity than that of g-C₃N₄ with structural distortion. As can be seen from Figure S21b and c, the time for the photodegradation of 80% of RhB molecules for CN-12 and F-CN-12 is about 24 min and 17 min, respectively, while these values decrease with the increasing of heat treatment time. After heating of the sample for up to 96 hours, the activity of both disorder-engineered g-C₃N₄ and disorder-engineered F-doped g-C₃N₄ for the photodegradation of RhB molecules are stable, which need only about 6 min and 2 min for the degradation of 80% of RhB molecules under simulated sun light, respectively.

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