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Supporting Information

One-step exfoliation and fluorination of g-C_3N_4 nanosheets with enhanced photocatalytic activities

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S1. Experimental Section

To confirm the exfoliation and fluorination process, a group of control experiment was conducted. In the control experiments, the procedure was almost the same as the method in the main text. However, the differences were the amount of NH_4F changed from 0 to 2.0 g and the reaction time changed from 2 h to 16 h. As shown in Fig. S1a, it was find that no exfoliation occurred when there was no NH_4F in the system. And if we increased the amount of NH_4F or prolonged the reaction time, wrinkled or broken F-C_3N_4 nanosheets could be obtained.

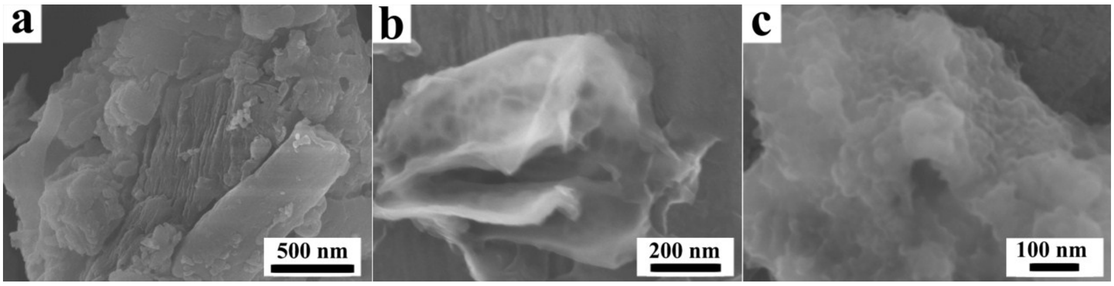

Fig. S1. SEM images of products obtained by without NH_4F (a), fluorination for 4h (b) and 16 h (c).

S2. High Resolution Transmission Electron Microscopy (HRTEM) image of F-C_3N_4 nanosheets

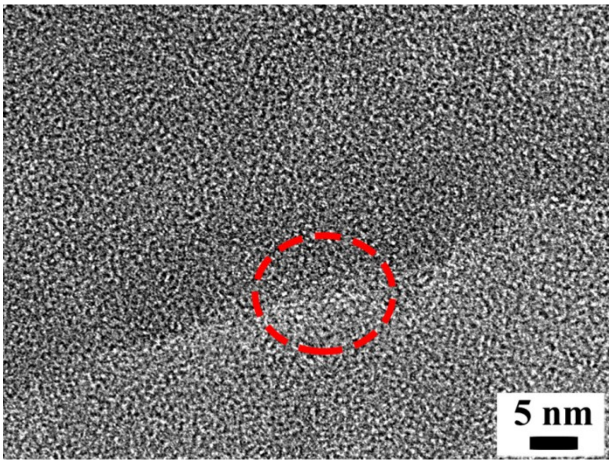

Fig. S2. High Resolution Transmission Electron Microscopy (HRTEM) image of F-C_3N_4 nanosheets.

S3. Influence of fluorination time and illuminants to the photocatalytic performance

The control experiments showed that the photocatalytic performance of F-C_3N_4 nanosheets could be influenced by the fluorination time. As shown in Fig. S3, the samples were fluorinated for 0, 2, 4, 8 and 16 h and noted as 1, 2, 3, 4 and 5, respectively. Firstly, the H_2 evolution rate was improved with the increase of fluorination time, which could be caused by the thinner and thinner nanosheets. Then, the rate of H_2 evolution achieved the maximum when the fluorination time was 8 h. The rates of H_2 evolution at the optimum condition were 1803.4 μmol h^{-1} g^{-1} under UV-visible light irradiation and 477.6 μmol h^{-1} g^{-1} under visible light irradiation. The F-C_3N_4 nanosheets showed a superior ability to the bulk g-C_3N_4 in the photocatalytic performance under both UV-visible light and only visible light irradiation. After that, excess fluorination could break the structure of F-C_3N_4 nanosheets, and the rates of H_2 evolution were decreased.

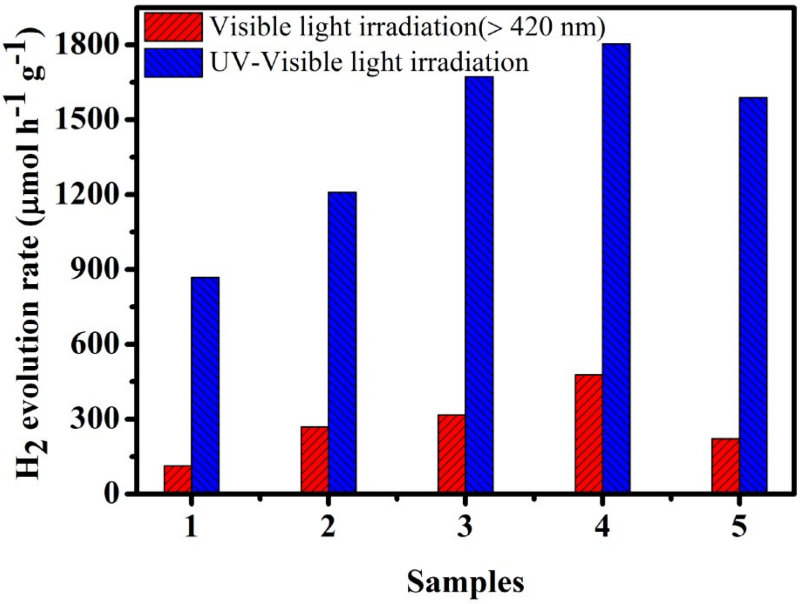

Fig. S3. Influence of fluorination time and illuminants to the photocatalytic performance.

S4 Optical images of bulk g-C_3N_4 and F-C_3N_4 nanosheets

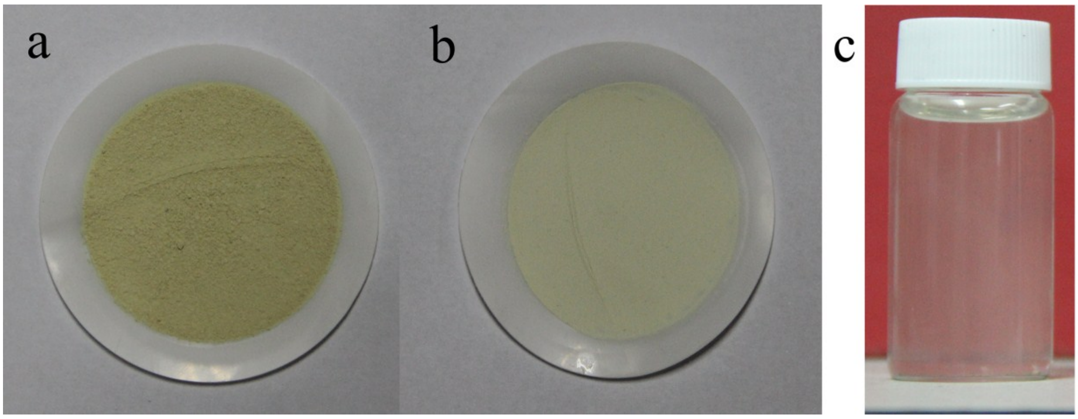

Fig. S4. Optical images of bulk g-C_3N_4 (a), F-C_3N_4 nanosheets (b) and F-C_3N_4 suspensions after centrifuging (c).

S5. Magnetic properties of bulk g-C_3N_4 and F-C_3N_4 nanosheets

The magnetic measurement was executed as a function of magnetic field (*M-H*) at room temperature with a maximum applied field of 10 K Oe by Superconducting Quantum Interference Device (SQUID). The diamagnetic contribution from the capsule and sample holder was mathematically subtracted. The changes of magnetization with the temperature are studied by applying magnetic field in the range of -10k Oe < H < 10k Oe at temperature ranging from 5K to 350K. As shown in Fig. S5a, temperature dependent of magnetization is demonstrated clearly at least up to 350 K. The enlargement of the hysteresis loops are shown in the Fig. S5b for more detailed and direct display. Obviously, M_s and corresponding H_C showed downward trend with the increasing of temperature up to 350 K. This characteristic make the as-prepared F-C_3N_4 nanosheets are quite promising for applications in spintronic devices.

In order to check the temperature dependence of the magnetization for the as-prepared F-C_3N_4 nanosheets, we carried out the ZFC and FC magnetization measurements at temperatures ranging from 5 to 300 K. As can be seen from the ZFC/FC curves, magnetization decreased sharply at low temperatures and then decreased gradually as the temperature increased. No blocking temperature is detected, indicating that there are no ferromagnetic clusters in the sample.[1] Small paramagnetic upturn only occurred below 25 K, this characteristic should be attributed to unreconstructed point defects and zigzag edges.[2] ZFC/FC curves show a distinct difference in this temperature range which revealing that antiferromagnetic correlation competes with ferromagnetic interactions as well as *FM* transition temperature above 350K.[3] The ZFC/FC curves overlap until the temperature reaches 350 K, which indicates the absence of superparamagnetism.[4]

ZFC/FC is a powerful technique that can indirectly detect any magnetic nanoclusters in the as-prepared F-C_3N_4 nanosheets that cannot be easily detected by XRD, EDS, or XPS measurements. The smooth and featureless ZFC/FC curves indicate the absence of any secondary or tiny parasitic magnetic phase, which is consistent with the inductively coupled plasma–atomic (ICP) results in the subsequent discussions. The ICP results (Table S1) show that less than 10 ppm of the transition metal impurities were detected. The M_s caused by transition metal impurities can be calculated at less than 1.3×10^{-6} emu/g, which is insufficient to affect the ferromagnetic signal of the as-prepared F-C_3N_4 nanosheets. On the basis of above analysis, the observed *FM* of the as-prepared F-C_3N_4 nanosheets can be mainly attributed to the topological fluorination.[5] Thus, the observed *FM* in the ultrathin metal-free F-C_3N_4 nanosheets must be intrinsic.

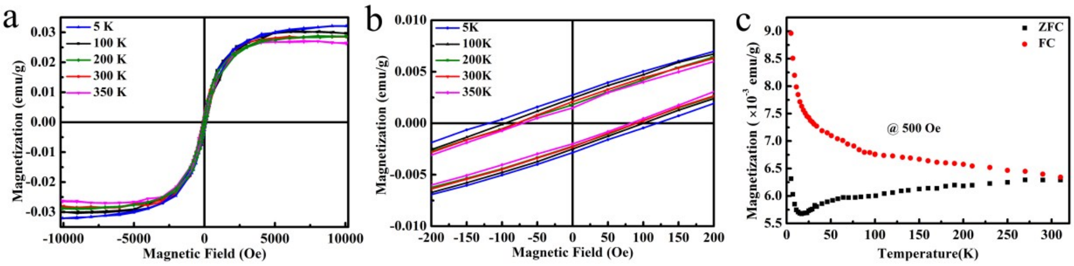

Fig. S5. Magnetic properties of F-C_3N_4 nanosheets. a) Hysteresis loops measured of F-C_3N_4 nanosheets for applied magnetic field between -10K Oe and 10K Oe at at 5 to 350K. b) Enlargement of the hysteresis loops of F-C_3N_4 nanosheets in the range of -500 Oe < H < 500 Oe. c) Temperature dependence of field-cooled (FC, solid red dot) and zero-field-cooled (ZFC, solid black squares) magnetization of F-C_3N_4 nanosheets for applied magnetic field at 500 Oe.

S6. Concentrations of transition metals Fe, Co, Ni and Mn in the bulk g-C_3N_4 and as-obtained F-CN nanosheets

Table S1. Concentrations of transition metals in the bulk g-C_3N_4 and as-obtained F-C_3N_4 nanosheets.

	Fe (ppm)	Co (ppm)	Ni (ppm)	Mn (ppm)
Bulk g-C_3N_4	1.2846	Not detected	0.0986	0.0952
F-C_3N_4 nanosheets	2.0054	Not detected	0.0790	0.7823

Magnetic property can be greatly influenced by the transition metal impurities, so it is necessary to detect the impurities of the starting materials and as-obtained samples by inductively coupled plasma-atomic (ICP) before measuring the magnetic of F-C_3N_4 nanosheets. From the data listed in the table S1, it can be seen that the total amount of possible magnetic impurities of Fe, Co, Ni and Mn are estimated at less than 10 ppm.

References

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