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

Electronic Supplementary Information

A new precursor to synthesize g-C_3N_4 with superior visible light absorption for photocatalytic application†

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Experimental Section

All chemicals used in the experimental section were analytical grade and used as received without further purification.

1. Materials

M-CN and TD-CN powder were prepared by heat treatment of melamine (Wako Pure Chemical Industries, Ltd., 99%) and thiourea dioxide (Wako Pure Chemical Industries, Ltd., 97%), respectively. A typical preparation process was as follows. Melamine in an alumina pot was heated to 550 °C in the speed of 10°C/min, and kept for 4 h in a muffle furnace (M-CN); thiourea dioxide in an alumina pot was heated to 450 °C in the speed of 10°C/min, and kept for 12 h in a muffle furnace (TD-CN).

Thin film electrodes of M-CN and TD-CN were deposited on the surfaces of FTO glass substrates by the electrophoresis method. The prepared samples (35 mg) were dissolved into the acetone (35 mL) for 1h ultrasonic, and then added 20 mg of iodine for 30 min ultrasonic. The samples were electroplated on the surface of the ITO glass with an area of 3 cm^2. The distance between the electrodes was fixed at 13 mm. The Plating voltage is 20 V, and the time of duration is 5 min for 3 times. After fabricating, the thin film electrodes were calcined at 300°C for 1 h.

2. Characterization

The crystalline phase of M-CN and TD-CN were characterized by using a powder X-ray diffraction (XRD) instrument (MiniFlex II, RigakuCo.) with CuKα (λ = 1.5418 Å) radiation (cathode voltage: 30 kV, current: 15 mA). The morphologies of the samples were observed by FESEM (JEOL, JSM-6701FONO). Nitrogen adsorption/desorption measurements were performed at 77 K using a Quantachrome Nova 4200e to calculate the specific surface area using the BET model. An absorption spectrum was acquired at room temperature with a UV–vis spectrometer (UV-2600, Shimadzu Co.). DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) was used to analyze the nature of the adsorbed species on the photocatalyst. The system consisted of an FTIR spectrometer (Jasco FT/IR-4200) equipped with a DRIFTS cell (Jasco DR-81 Diffuse Reflectance Attachment). An XPS experiment was carried on a Thermo ESCALAB 250Xi system at room temperature under Al Kα using monochromatic radiation and C1s peak (284.70 ± 0.1 eV) reference. A TG experiment was carried on a Thermo plus Evo II TG 8120.The background of XPS spectra was subtracted by the Shirley procedure and the peaks were fitted using the Gaussian-Lorentzian function.

3. Photoelectrochemical measurements

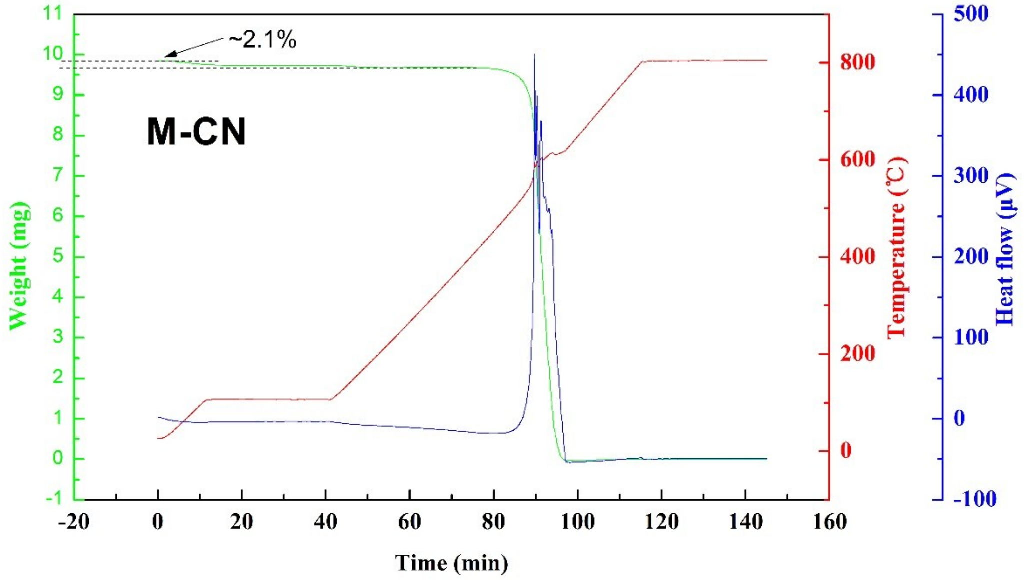
Photoelectrochemical measurements were performed with a homemade photoelectrochemical system. A 500 W Xe lamp was used as the irradiation source. Photocurrent was measured on an HSV-110 electrochemical workstation (Hokuto Denko). Photocurrent response measurements were conducted in 0.1 M Na_2SO_4 solution in a three-electrode system. Fluorine doped Tin Oxide (FTO) electrode with g-C_3N_4 was employed as the working electrode. A coiled Pt wire was used as the counter-electrode and a saturated Ag/AgCl as the reference electrode. The interval time of light-on and light-off is 2 s.

4. Evaluation of oxidation products

Photocatalytic activity of the samples was evaluated by photocatalytic decomposition of 2-propanol in gas phase. Samples powder (150 mg), which had completed extinction of incident radiation, was spread on a glass dish, and the glass dish was put into a Tedlar bag (AS ONE Co. Ltd.) with a volume of 125 mL mixed air (79% N_2, 21% O_2, <0.1 ppm of CO_2, 500 ppm of 2-propanol). After 2-h adsorption equilibrium in the dark, the photocatalysts were exposed under the visible light (LED, $\lambda = 435$ nm). The light intensity was fixed to 3 mW/cm^2. In the photocatalysis process, generation of carbon dioxide, acetone and consumption of 2-propanol were monitored by online gas chromatography (Agilent Technologies, 3000A Micro-GC, TCD detector) equipped with OV1 and PLOT-Q columns.

5. Computational methods

The DFT computations were performed by using the CASTEP module. Both the bulk crystalline cells and the atom positions of the pristine and co-doped g-C_3N_4 were optimized within the generalized gradient approximation (GGA) and the exchange–correlation functional of Perdew-Wang 91 (PW91). In order to describe the weak interaction between the graphitic-like layers of g-C3N4 more accurately, we use the DFT with the semi-empirical dispersion–correction scheme (DFT-D). The kinetic cut-off energy for the plane-wave basis set was chosen to be 540 eV, the Monkhorst-Pack k-point meshes were set as 3×3×1, and the ion–electron interactions were modeled by the ultrasoft pseudo-potential. The convergence criteria of the geometry optimization for the energy change, maximum-force, maximum stress, and maximum displacement tolerances were set to 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. The density of state of the pure and co-doped g-C_3N_4 systems were computed with the HSE06 functional, for which the kinetic cut-off energy was set at 600 eV. Other settings, such as the Monkhorst–Pack k-point meshes, norm conserving pseudo-potential, and the convergence criteria, were the same as for geometry optimization.



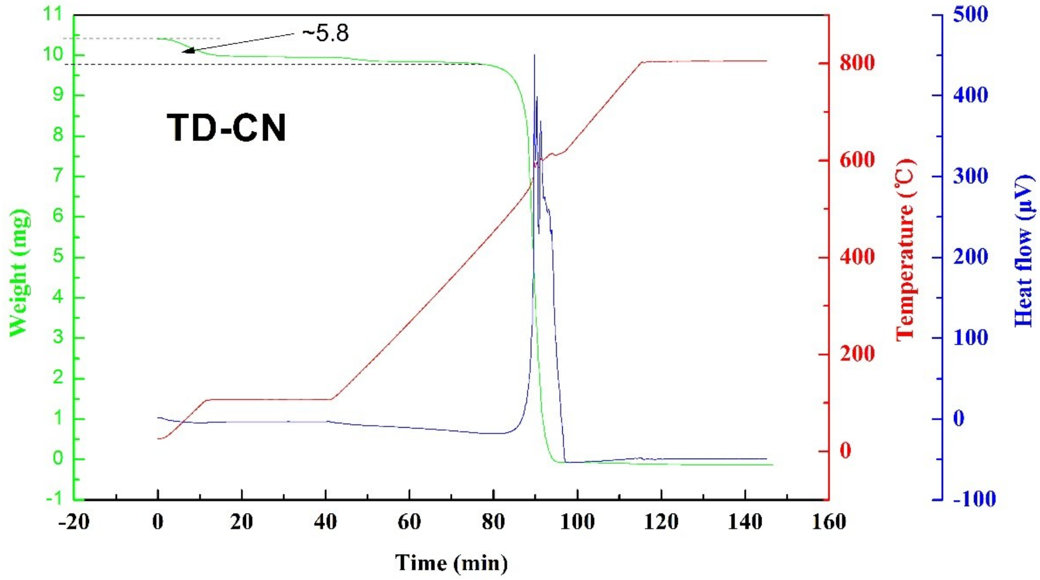


Fig. S1 TG results

Both of samples' decomposition temperature is around 520 °C. The different property of TD-CN and M-CN between room temperature and decomposition temperature. Mass loss of M-CN and TD-CN is ~2.1% and ~5.8%, respectively. Around 100°C, the absorbed water is lost, which is in agreement with XPS results. Mass loss of M-CN is concentrated upon ~100°C, while TD-CN owns two-stage mass loss. Range of 100°C and 400°C could be attributed to sulphide and defects portion.

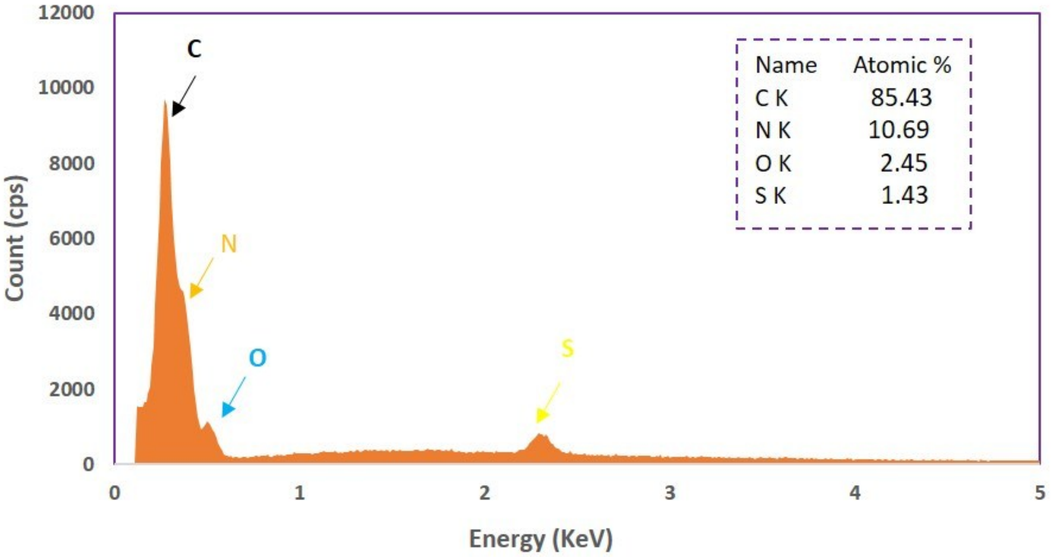


Fig. S2 EDS result of TD-CN

The EDS result of indicate that C, N, O and S peaks could be detected and no other impurity peaks could be observed. Although we can't confirmed the accuracy contents of C and N (because conducting resin owns C and N components.). The contents of O and S is relatively accurate. Compared with the ratio of S (0.33%) and O (1.96%) from XPS, EDS result shows 1.43% and 2.45%. These results indicate that S and O not only on the surface but also in bulk.

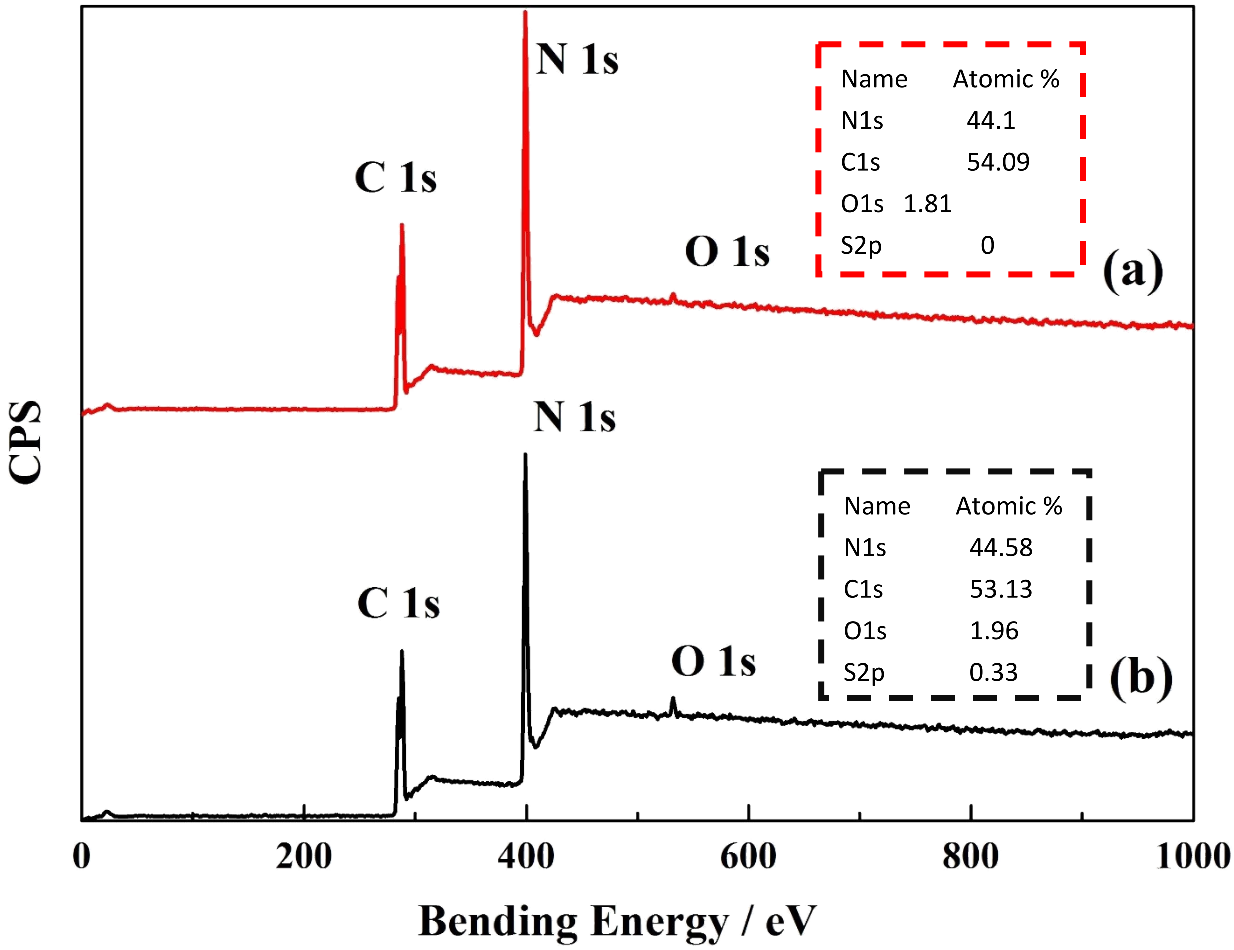
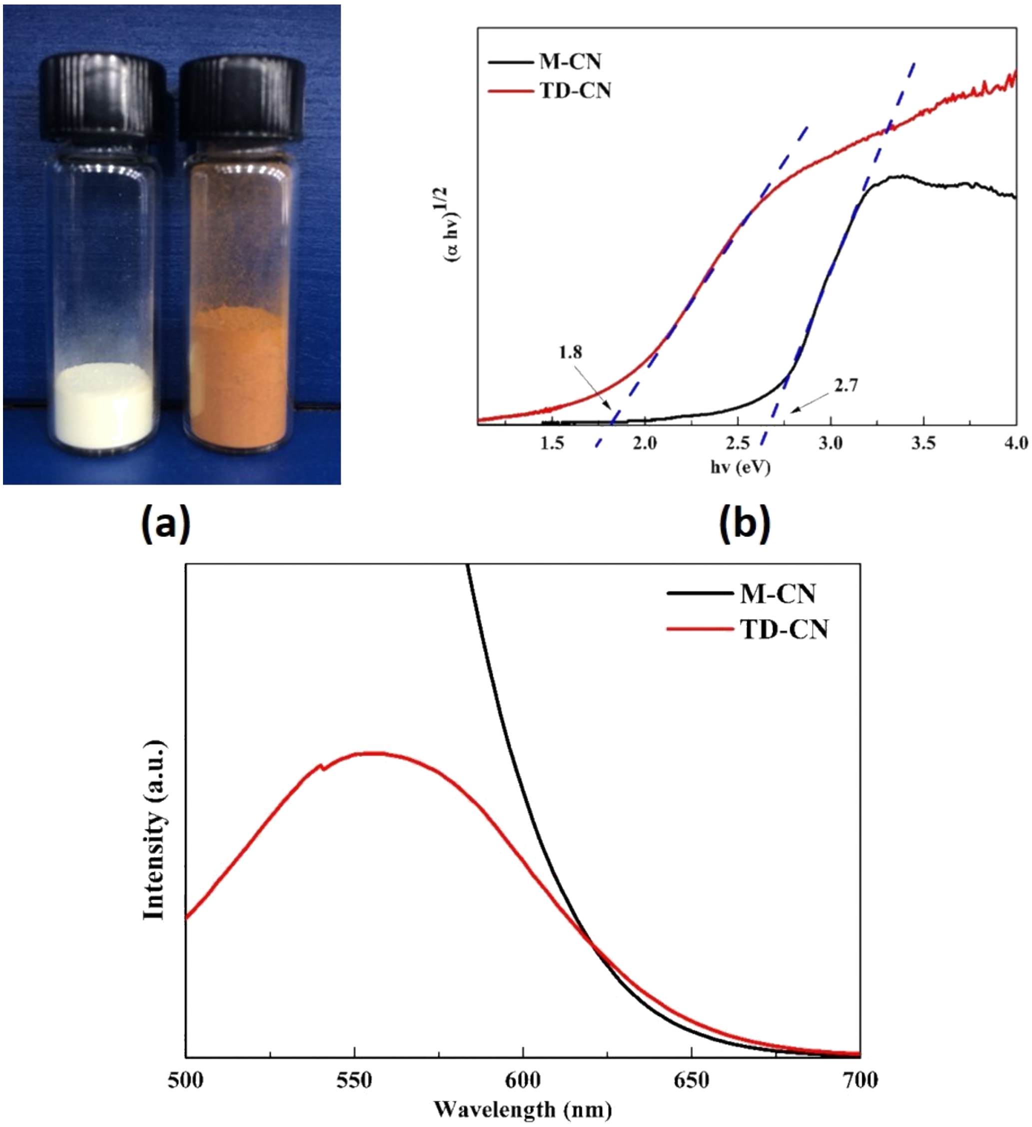


Fig. S3 XPS survey spectra of (a) M-CN and (b) TD-CN, insets are element content analysis results.



(a)

(b)

(c)

Fig. S4 (a) photograph of samples (The sample mass was also 0.5 g.) (b) Kubelka–Munk functional UV-vis spectra (c) PL spectra (435 nm excitation at room temperature).

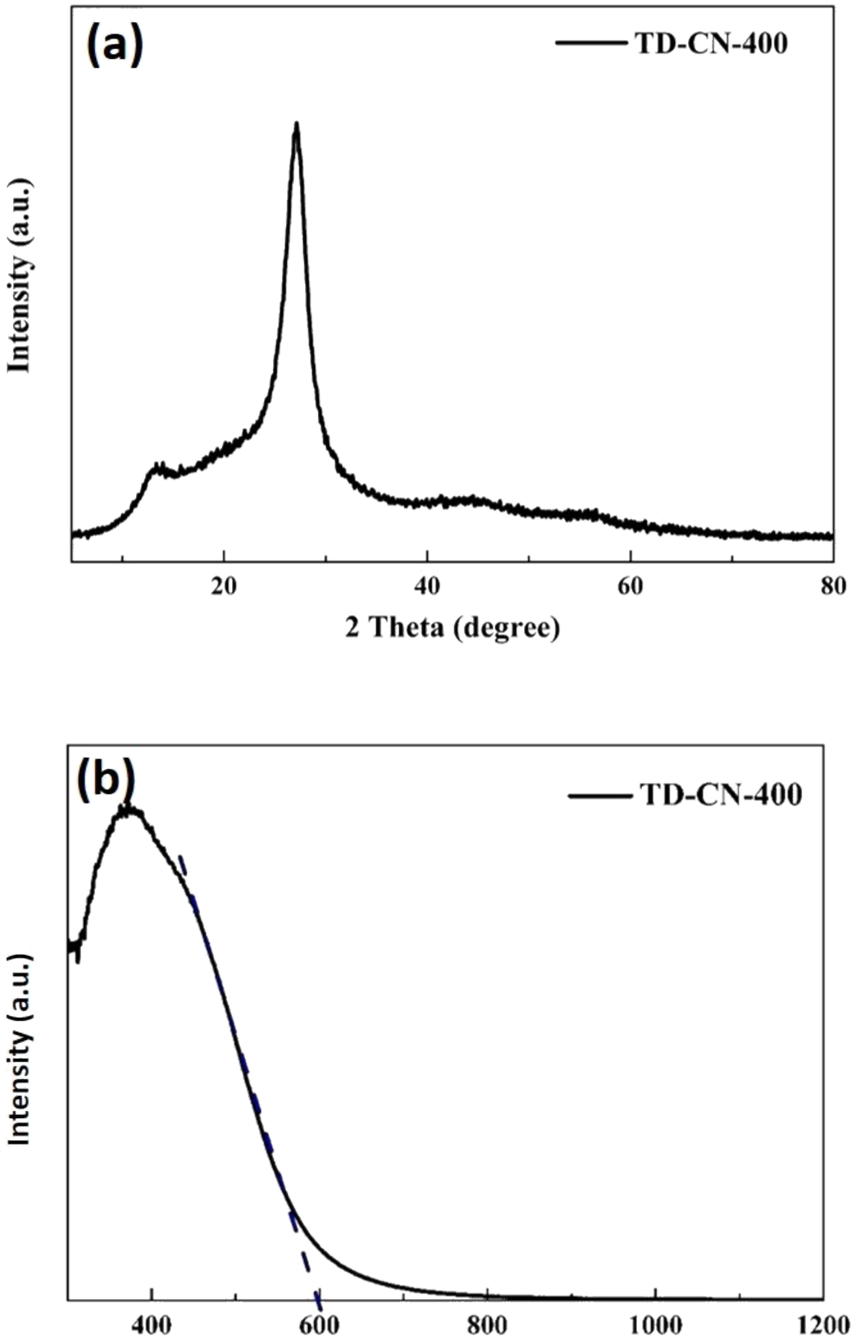


Fig. S5 TD-CN prepared at 400°C calcination temperature.

(a) XRD pattern (b) Kubelka–Munk functional UV-vis spectrum.

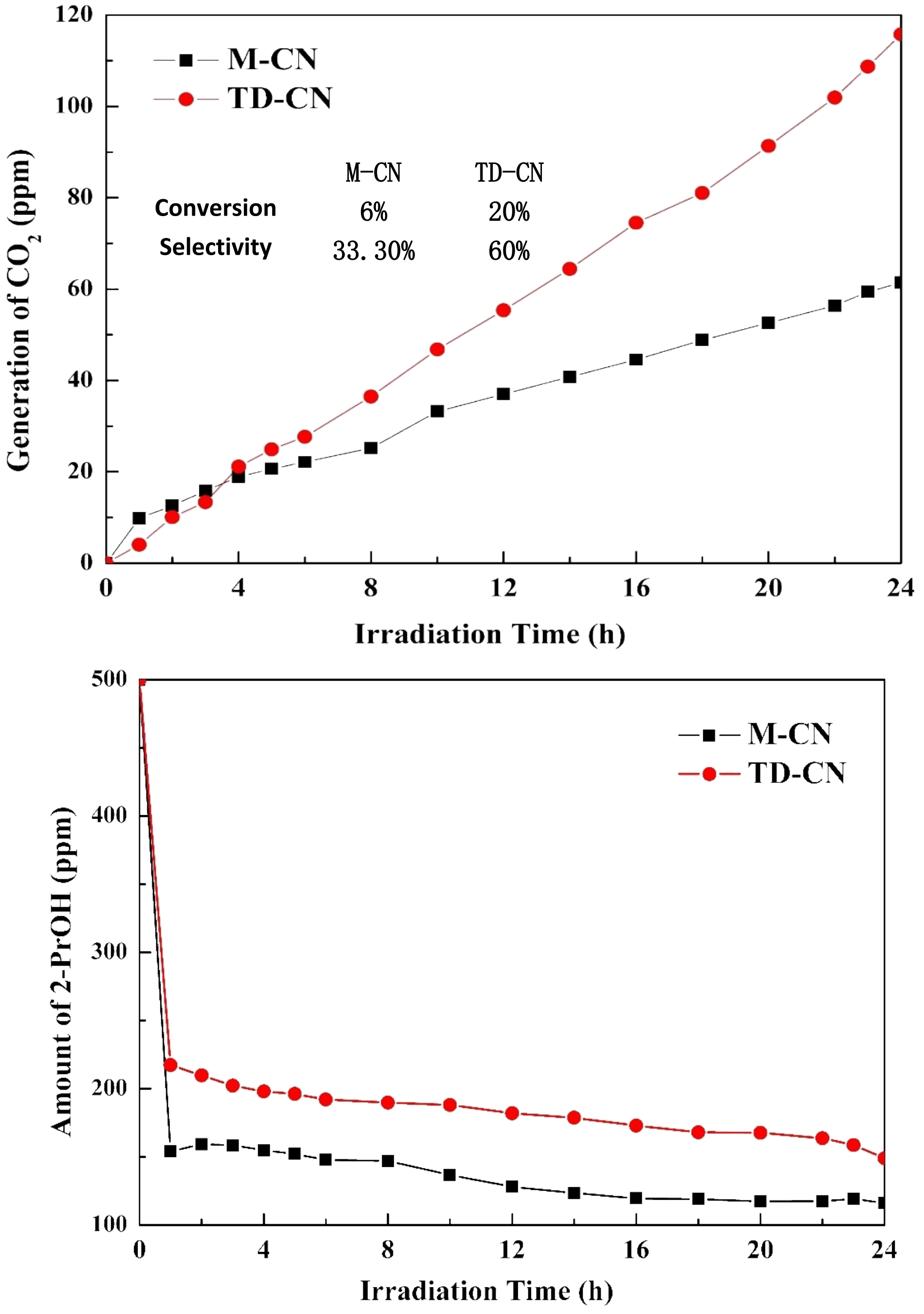


Fig. S6 generation of CO_2 and amount of 2-PrOH

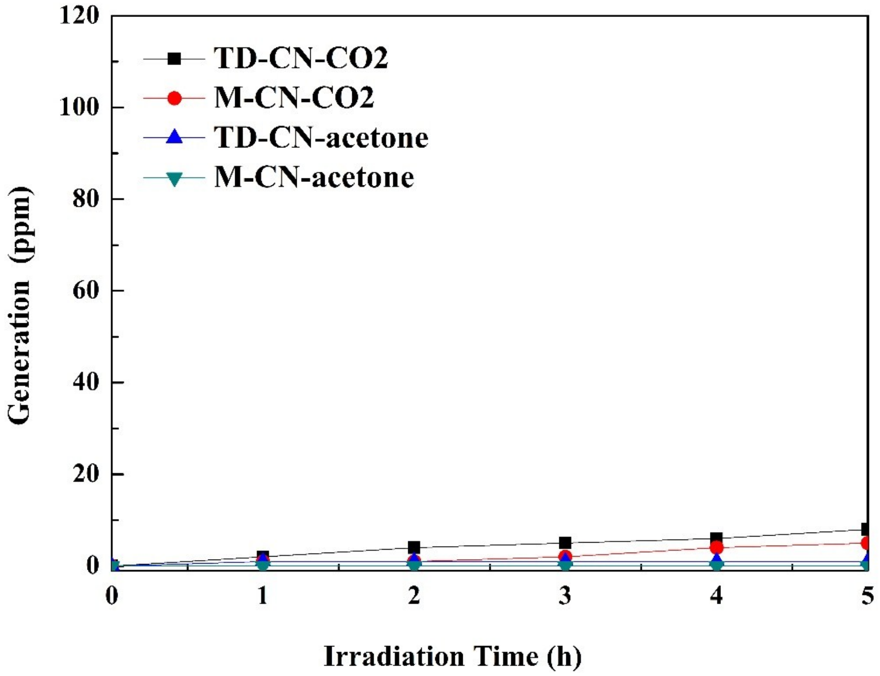


Fig. S7 Blank experiments of both samples.

The blank experiments results that both samples are almost no activity without light irradiation. The generation of acetone was ~0 ppm, while about ~10 ppm CO_2 generated. It could be from absorbed CO_2 in air.

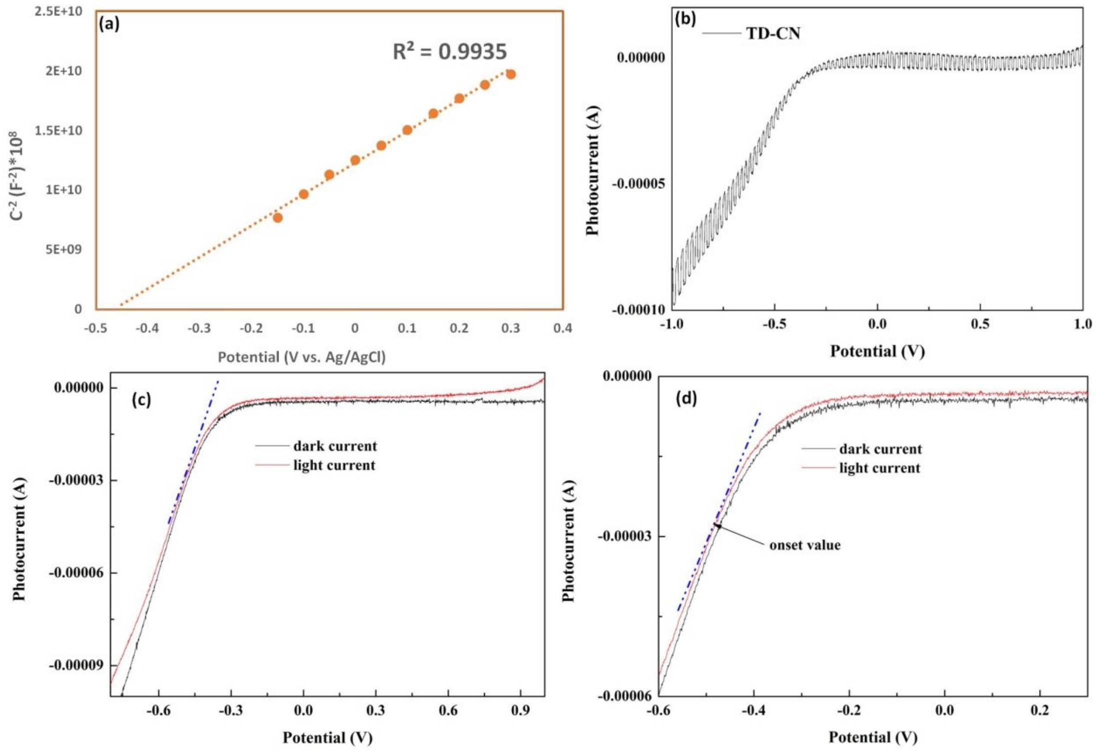


Fig. S8 Energy band test of TD-CN (a) Mott-Schottky plots, the frequency is 500 Hz, (b) long range of photocurrent response, (c) dark current, (d) enlarged image of onset potential spectra.

Mott-Schottky plots shows that flat band is ~-0.48 V, and the correlation coefficient R^2 is 0.9935. This means that the linear fit is correct. The long range of photocurrent result indicates that TD-CN has both plus or minus bias response. In order to further improve the veracity of flat band, we tested it onset potential of photocurrent response. The onset potential is determined by the potential when the plot starts to deviate from the linear region as indicated by the arrow. It was also around -0.48 V. So we could concluded that the rough conduction band (C.B.) is -0.48.

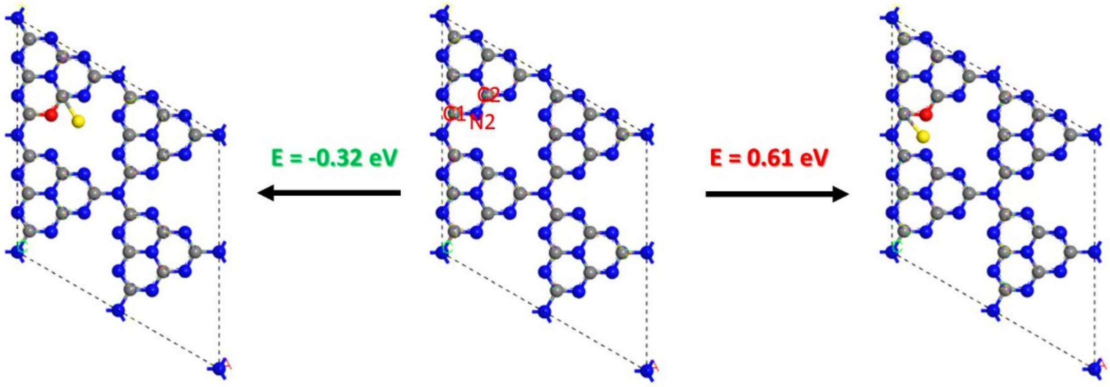


Fig. S9 two possibilities of Sulphur interstitial doping models and their respective formation energy. (Black and blue spheres represent the C and N atoms, respectively.)

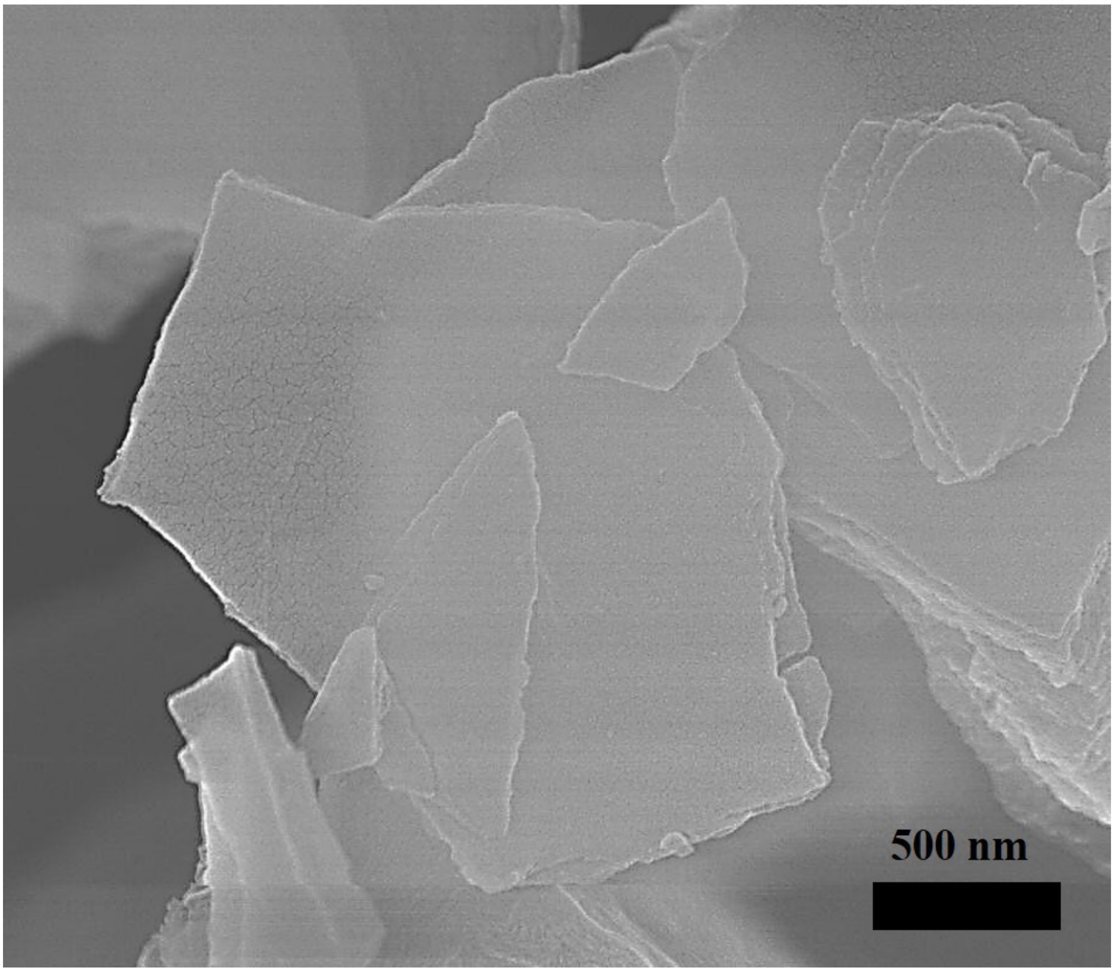


Fig. S10 SEM image of TD-CN specific section