

Supporting Information

High alkalinity boosts visible light driven H₂ evolution activity of g-C₃N₄ in aqueous methanol

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Experimental

Chemicals. Dicyandiamide (DCDA 99.5+%) were purchased from ACROS Organics. Urea (99.5+%), methanol (99.8+%), sodium sulphate (Na₂SO₄ 99.0+%) were purchased from Aldrich. Thiourea (99.0+%) were purchased from Alfa Aesar. Sodium hydroxide (NaOH 99.9+%), potassium hydroxide (KOH 87.2+%), acetone (99.7+%), isopropanol (99.8+%) were purchased from Fisher Scientific. Water was purified to the resistivity of 18 MΩ·cm using an ultrapure water system (NANOpure Infinity).

Synthesis. The bulk g-C₃N₄ photocatalysts were synthesized through a facile calcination process. In detail, different amounts of precursor (DCDA, urea or/and thiourea) were added in to a crucible with cover, heated in a tubular furnace to 520 °C in 3h and kept at that temperature for 2h. The products were collected and ground into powder in a ceramic mortar for at least 10 min. For the sake of simplicity, D52 (U52/T52) stands for the sample prepared by calcination of DCDA (urea/thiourea) at 520 °C. The sample prepared from the mixture of urea and thiourea is denoted as UT52.

The ultrathin g-C₃N₄ nanosheets used for electrochemical measurement were obtained by liquid exfoliating of as prepared bulk g-C₃N₄ (D52) in water.¹ In detail, 100 mg bulk D52 was dispersed in 150 mL water, and then maintained in ultrasound for 24 h. The water in the ultrasonic generator was changed by cold water to avoid too hot temperature. The obtained suspension was centrifuged at 1000 rpm for 2 min to remove the precipitate.

Thin films for SPV measurements were prepared by drop coating 0.1 mL suspension on indium tin oxide (ITO)-coated glass (ca. 1.0 cm²) at room temperature, with Parafilm restricting the area. Before SPV test, the dried films were heated on the hot plate at 100 °C for 10 min. The suspension was made by adding as-prepared samples (5 mg) into water (3 mL) and further maintaining it in ultrasound for 1 h.

The film of D52 nanosheets, which was used for electrochemical experiment, were fabricated by first drop-coating 0.1 mL nanosheets suspension (ca. 0.5 g/L) on half of fluorine-doped tin oxide (FTO) glasses (1.0 cm x 2.0 cm) at room temperature for three times and further heating at 400 °C for 3 h to stabilize it.

Characterizations. UV-Vis absorption spectra were recorded with a Thermo Scientific Evolution 220 UV-Vis spectrometer, using the thick films fixed on white polytetrafluoroethylene (PTFE) thread seal tape. The Tauc plots were obtained through two formulae: $R = 10^{-A}$ and $F(R) = (1 - R)^2 / (2R)$, where A , R and $F(R)$ stand for absorbance, relative reflectance and Kubelka-Munk function, respectively.^{2,3}

Powder X-ray diffraction (XRD) patterns were conducted with a Scintag XRD ($\lambda = 0.154$ nm) at -45 kV and 40 mA, equipped with tube slit divergence (2 mm), scatter (4 mm), column scatter (0.5 mm), and receiving (0.2 mm) slits.

Fourier transform infrared reflection (FTIR) spectra were obtained with the IR tester (BRUKER-Alpha) and software (OPUS 6.5). The samples were not modified with KBr before measurements.

Transmission electron microscopy (TEM) images were taken with a Philips CM-12 TEM instrument with accelerating voltage of 120 kV. To prepare the sample, the above mentioned suspension was diluted, ultrasound-treated for 1h. After that, the particle-dispersed solution was drop-casted onto a carbon-coated copper grid, followed by air drying.

Surface photovoltage (SPV) measurements were performed by using a vibrating gold Kelvin probe (Delta PHI Besocke) mounted inside a home-built vacuum chamber ($< 5 \times 10^{-4}$ mbar). The above mentioned films were illuminated with monochromatic light from a 175 W Xe lamp filtered through an Oriel Cornerstone 130 monochromator (light intensity range: 0.1-0.3 mW/cm²). The obtained SPV spectra were corrected by subtracting a dark scan background recorded prior to the light measurement.

Photocatalytic H₂ evolution was determined by irradiating 30 mg of photocatalyst dispersed in 100 mL methanol aqueous solution (20% by volume). The pH-dependent experiments were adjusted with KOH. Irradiation was performed in a quartz round bottom flask using light from a 300 W Xe arc lamp (PerkinElmer PE300BUV, for spectrum see Figure S7)) equipped with a 400 nm long-pass filter (1 M NaNO₂) which gave 380 mW/cm² at the flask surface as measured by a GaAsP photodetector. Before the reaction, platinum (1.0 w. %) was first photodeposited in situ on the photocatalysts under full spectrum irradiation for 2 hours from the precursor H₂PtCl₆·6H₂O, and then was directly used for H₂ evolution. The air-tight irradiation system connects a vacuum pump and a gas chromatograph (Varian 3800: 60/80 Å molecular sieve column and thermal conductivity detector) to quantify the amount of gas evolved. Prior to irradiation, the flask was evacuated down to 60 torr and purged with argon gas for three times to remove the atmosphere above the solution. No H₂ evolution was detected in the absence of photocatalysts or/and light irradiation.

Apparent quantum yield (AQY) was measured using a 400 nm LED (LZC-00UA00 of LedEngin, Inc.: 730 mW/cm² x 3.24 cm² at the outlet) as the light source and the photometer (IL1400BL) as the detector. It was defined by equation: $AQY = 2N_H/N_P$, where N_H is the number of obtained H₂ molecules and N_P is the number of incident photons

Photoelectrochemistry properties were measured in a 3-electrode cell with a Pt counter electrode and a saturated calomel reference electrode (SCE) connected to the cell through a KCl salt bridge. The cell was first filled with 40 mL of 0.2 M Na₂SO₄, and then exchanged 5 mL with methanol (or 1M NaOH) for the followed measurements. Before every scan, the solution was purged with N₂ for 10 min to remove the O₂ inside. The data was collected by a potentiostat (Gamry Reference 600) under light illumination (60 mW/cm² at the film surface) from a Xe lamp with optical fibre as the transmitter. The reference potential was calibrated using the solution of K₃[Fe(CN)₆] (redox potential: +0.358 V vs. RHE).

Additional Figure

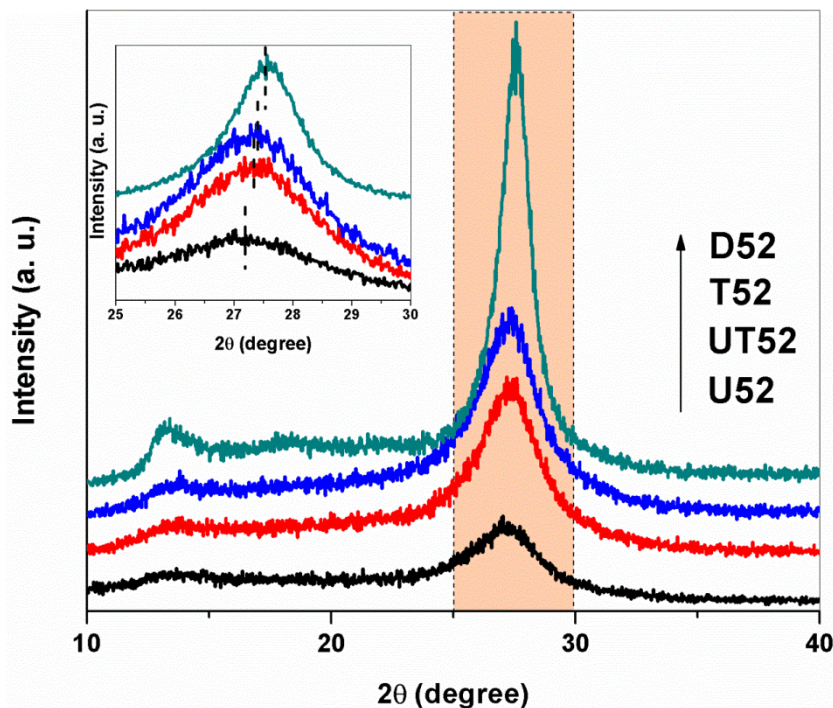


Fig. S1. Powder XRD patterns of samples U52, UT52, T52 and D52. The inset is the detailed patterns around the strongest diffraction peaks.

The XRD patterns of T52 and UT52 was similar, because UT52 contains large proportion of $g\text{-C}_3\text{N}_4$ from the condensation of thiourea. The larger productivity of thiourea (8.5 w. %) than urea (4.4 w. %) could account for this. There is a trend of XRD peak intensity: $D52 > T52 > UT52 > U52$, indicating that the crystallization becomes worse for the precursor thiourea/urea. Moreover, the magnified region (inset) features a low-angle shift of peak position from D52 to U52, meaning a widened interlayer distance for U52. This may be caused by the additional oxygen removal in the condensation process of urea, and it can also result in porous morphology with large special surface area as reported.⁴

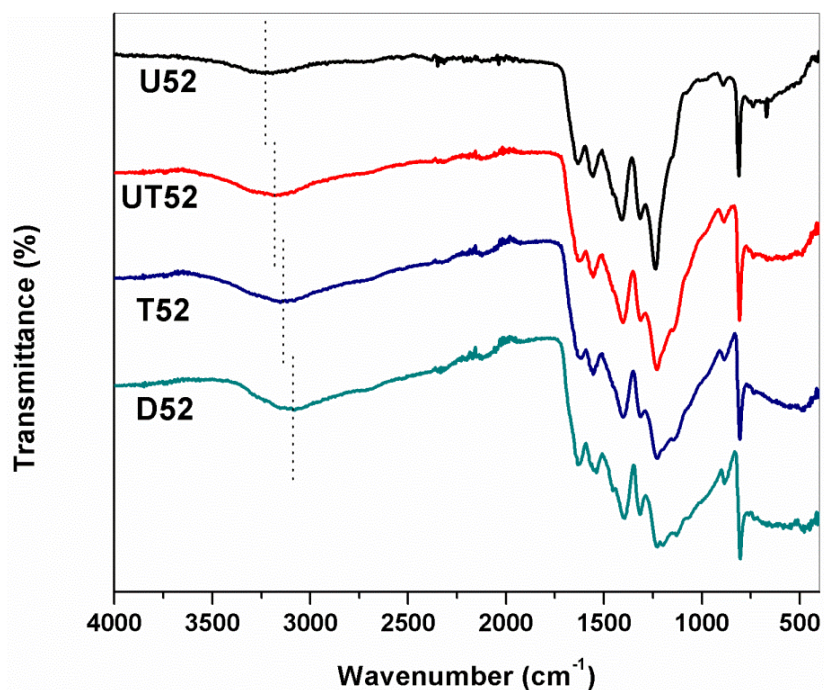


Fig. S2. FTIR spectra of samples U52, UT52, T52 and D52.

The characteristic absorption bands in the region of around 800 cm^{-1} and $1200\text{--}1700\text{ cm}^{-1}$, corresponding to the breathing mode and stretching vibration of $g\text{-C}_3\text{N}_4$, can be observed for all the samples from different precursors. A slight absorption shift presented in the region near 3000 cm^{-1} , manifesting the environmental difference of amino/imino groups. It should be noted that the sample UT52 had a peak center between that of U52 and T52. This may be an evidence for the junction structure.

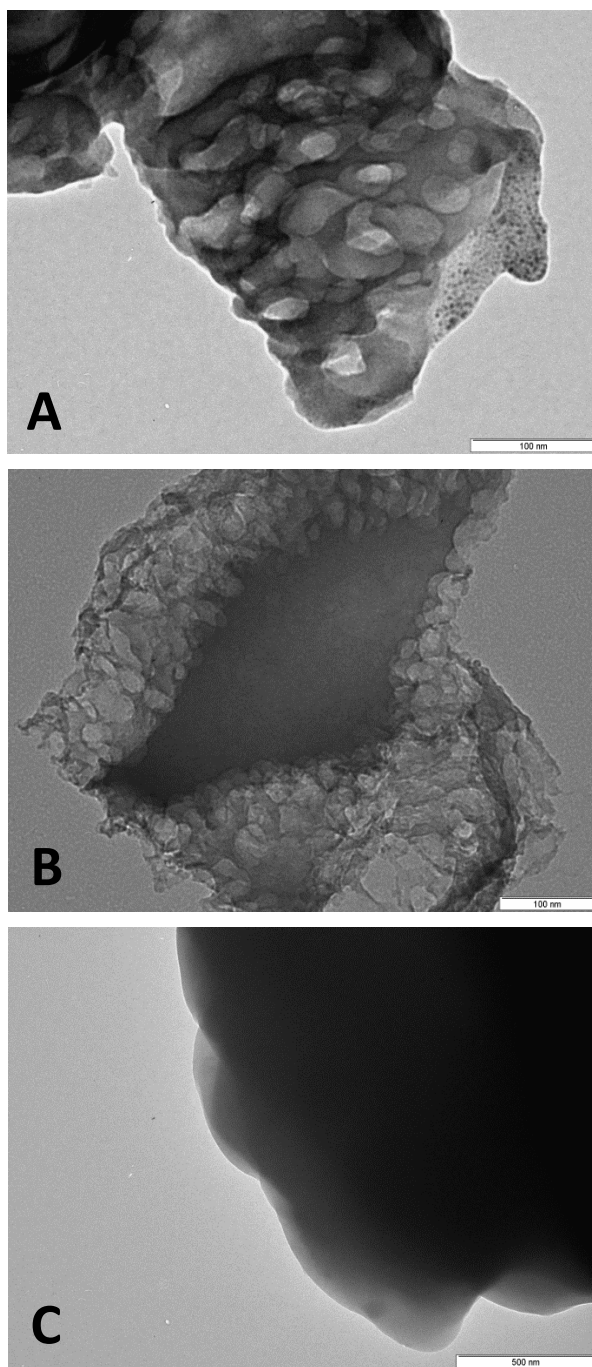


Fig. S3. TEM images for (A) U52, (B) UT52 and (C) T52.

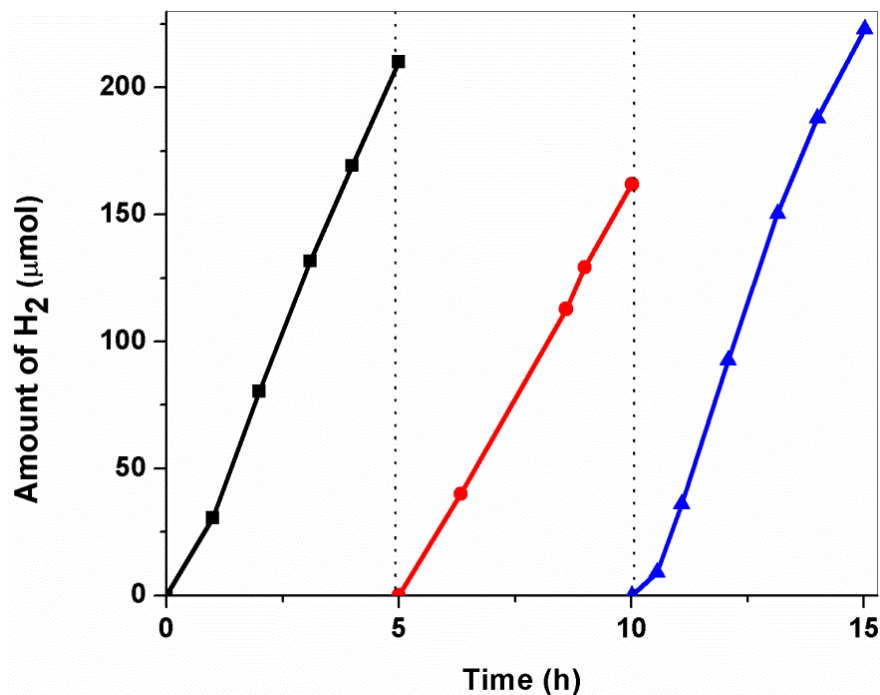


Fig. S4. Long-time runs of photocatalytic H₂ evolution over D52 (30 mg) in methanol (20 vol. %) aqueous solution at pH=13.3 under visible light ($\lambda > 400$ nm) irradiation. Evacuation of the gas space was performed every five hours. Calculated turnover number: $594 \mu\text{mol H}_2 / 326 \mu\text{mol photocatalyst (30 mg)} = 1.82$

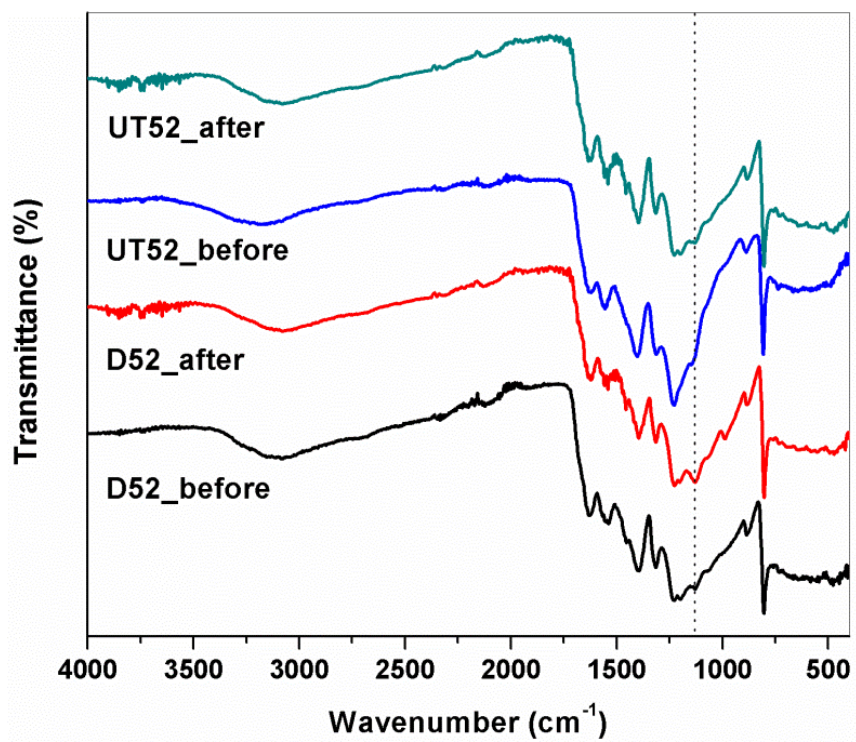


Fig. S5. FTIR spectra of D52 and UT52 before/after the AQY measurements.

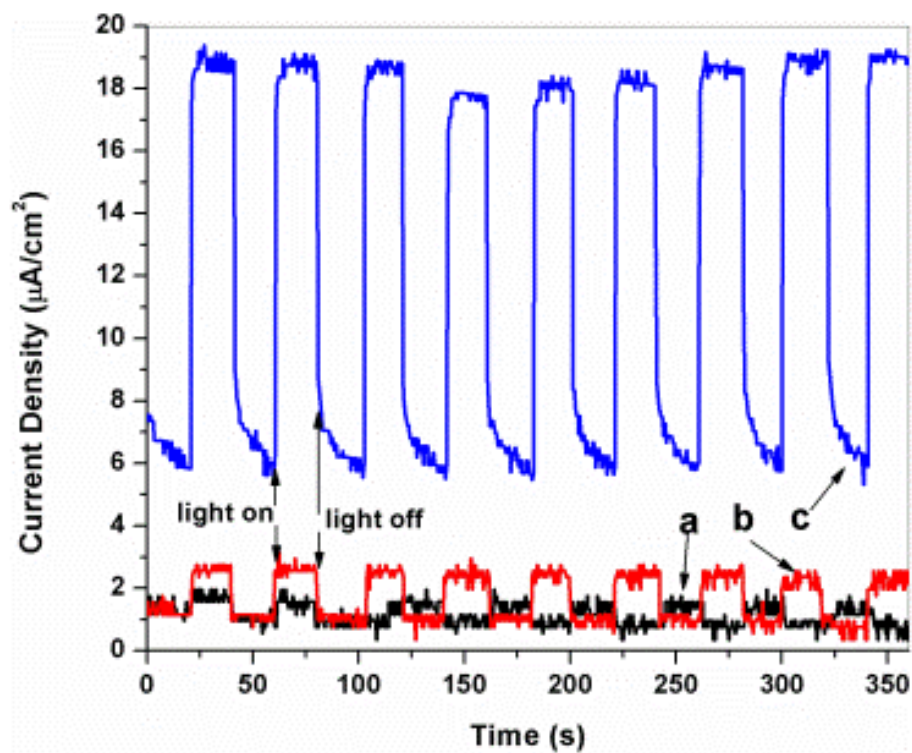


Fig. S6. Chronoamperometry (0.80 V vs. SCE) scans of the D52 film, respectively, in different solutions with/without methanol or NaOH (pH=5.6, 5.7 and 12.8 for [a] D52, [b] D52/MeOH and [c] D52/MeOH/NaOH, respectively).

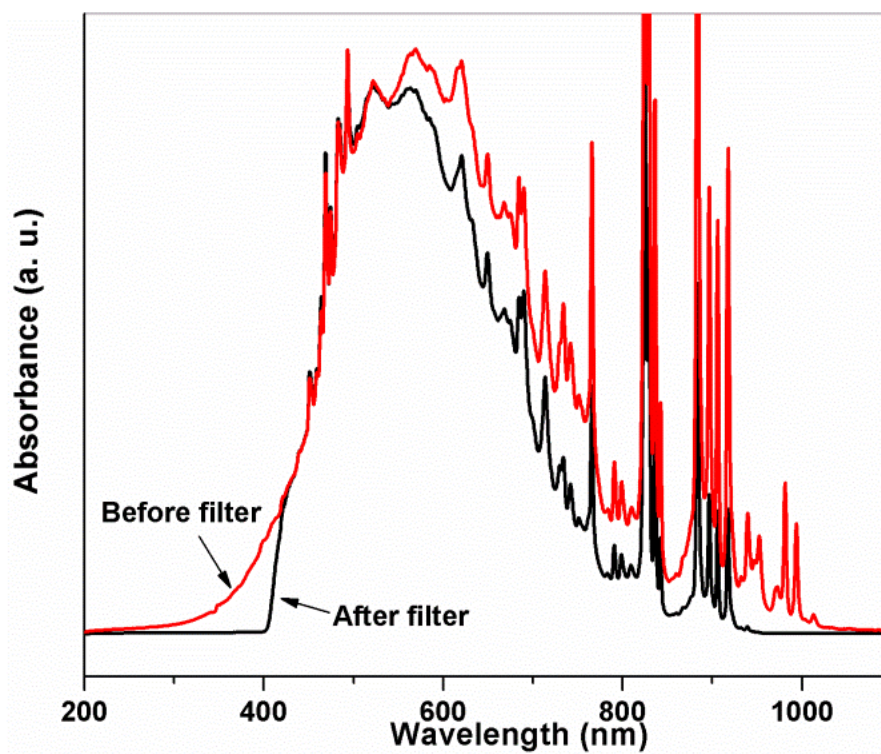


Figure S7. Xe lamp emission spectrum before/after NaNO₂ filter.

Supporting References:

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4. Y. Zhang, J. Liu, G. Wu and W. Chen, *Nanoscale*, 2012, **4**, 5300.