

Supporting Information

A General Strategy via Chemically Covalent Combination for Constructing Heterostructured Catalysts with Enhanced Photocatalytic Hydrogen Evolution

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Experimental section

Materials

Thiourea (99%), 1,4-dicyanobenzene (98%), trichloromethane (99.5%) and anhydrous ZnCl_2 (98%) were obtained from Aldrich. 4-aminobenzoic acid (99%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl, 98.5%), 1-hydroxybenzotriazole (HOBT, 97%), N,N-diisopropylethylamine (DIPEA, 99%), trifluoromethanesulfonic acid (98%) and sodium dodecylbenzenesulfonate (SDBS, 97%) were acquired from Macklin. All of the chemicals were commercially obtained and used without further purification.

Synthesis of CN nanosheets

The CN nanosheets were synthesized via a thermal oxidation method according to our previous work. Bulk CN was obtained by heating thiourea at 550 °C for 2 h. The CN nanosheets were synthesized by two-step thermal strip oxidation method. First, bulk CN powders were kept in an open ceramic at 500 °C for 2 h with a heating rate of 2 °C/min, and then repeat the previous step again. The final light yellow powder of CN nanosheets was obtained.

Synthesis of two-dimensional covalent triazine frameworks (2D-CTF-1)

CTF was synthesized according to the previously reported method. Typically, trifluoromethanesulfonic acid (19.96 g, 133.0 mmol, 4 eq) was added into a pre-dried three-neck round bottom flask containing CHCl_3 (30 mL) under inert gas atmosphere. Then, 1,4-dicyanobenzene (4.26 g, 33.25 mmol) dissolved in CHCl_3 (200 mL) was slowly dropwised into above resulted mixture at 0 °C under stirring. The mixture was stirred for 2 h at 0 °C and then heated to 40 °C for 48 h. A solid precipitate turned from colorless to yellow was formed. After cooled down to room temperature, the solid precipitate was rapidly added to 660 mL of deionized water containing 34 mL of ammonia solution (25 %), and then continuously stirred for 2 h. The precipitate was obtained by filtration and washed successively with deionized water, ethanol, acetone and chloroform. The yellow product was dried under vacuum for 12 h at 120 °C. The yellow precipitate regards as Pre-CTF. Pre-CTF (2.10 g, 16.39 mmol, 1 eq) was thoroughly mixed with ZnCl_2 (1.79 g, 13.11 mmol, 0.8 eq) in an inert argon atmosphere. This large batch of starting reaction mixture was evenly separated

into 6 parts which were each transferred to a porcelain crucible with lid and stored in a closed storage box to maintain the inert argon atmosphere. After preheating the argon oven for 30 min under a regulated argon flow of 2.5 °C/min to 400 °C, the crucibles were quickly placed into the argon oven and heated at 400 °C for 10 min. The crucibles were immediately removed from the hot oven and allowed to quickly cool down under argon atmosphere. The crude products were grounded and stirred in deionized water (150 mL) for 12 h at 60 °C, filtered and washed thoroughly with water to remove the majority of the salt. The mixtures were further stirred in 0.1 M HCl (150 mL) for 12 h at 60 °C to remove the residual ZnCl₂, filtered and subsequently washed with water and THF. The product was dried under vacuum for 12 h at 150 °C.

Synthesis of benzoic acid functionalization of CTF-1 nanosheets (B-CTF-1)

Benzoic acid functionalized B-CTF-1 was prepared through a diazo-type reaction. First, sodium diazonium was prepared according to the reported literature. sodium hydroxide (280 mg) and 4-aminobenzoic acid (960 mg) were dissolved into water (80 mL), and stirred to complete dissolution. Then, sodium nitrite (526 mg) was slowly added to the above solution at about 0 °C in ice bath. Subsequently, the solution was rapidly added to HCl solution (20%, 6 mL), and stirred for 45 min. Second, the above prepared CTF-1 nanosheets was added to deionized water containing 1 wt.% aqueous SDBS, and treated by ultrasound for 1 h. The as-synthesized sodium diazonium was added to the above suspension solution of CTF-1 nanosheets, and stirred for 4 h at about 0 °C in ice bath. Finally, the solution was filtered and subsequently washed several times with distilled water, ethanol, DMF, and acetone, respectively. The final powder of B-CTF-1 was dried at 60 °C for 12 h under vacuum.

Synthesis of metal-free heterostructured CNF composites

A certain amount of CN nanosheets and B-CTF-1 powder was placed into round bottom flask with 5 mL DMF. A uniform suspension was obtained by bath sonication under an inert atmosphere. 20 mg EDC·HCl and 20 mg HOBt were added into the above suspension with 300 µL DIPEA, and stirred at room temperature for 48 h under in inert atmosphere. A solid product obtained by filtration and subsequently washed with excess amounts of DMF and water to remove by-products. Finally, the samples were dried at 60 °C under vacuum.

Hereafter, the obtained samples of CN/B-CTF-1 composed of 5, 10, 15, and 20% B-CTF-1 were denoted as 5CNF, 10CNF, 15CNF, and 20CNF, respectively.

Synthesis of conventional heterostructured 10%CN/CTF-1 (10CN/F), 10%CN/B-CTF-1 (10CN/BF) hybrids

The 10%CN/CTF-1 and 10%CN/B-CTF-1 represent the composite catalysts, among which CN was combined with CTF-1 and B-CTF-1 via weak interactions but not covalent bonds of amide (-CONH-), respectively. The synthetic processes of 10%CN/CTF-1 and 10%CN/B-CTF-1 are similar to that of 10CNF except for the use of condensation agent. The 10%CN/CTF-1 and 10%CN/B-CTF-1 were denoted as 10CN/F and 10CN/BF, respectively.

Synthesis of aldehyde groups functionalized CTF-1 nanosheets (A-CTF-1)

As shown in Scheme S1, the CTF-1 (100 mg) was sonicated for 1 h to facilitate exfoliation in N,N'-dimethylformamide solvent before functionalization. 100 mg 4-Iodobenzaldehyde ($\geq 96.0\%$) was dissolved in N,N'-dimethylformamide (50 mL) under stirring. And the exfoliated CTF-1 was added into the above solution of 4-Iodobenzaldehyde and then stirred for 72 h at room temperature. The precipitate was separated by centrifugation and then washed with water, N,N'-dimethylformamide and ethanol to remove unreacted reagents, organic by-products and inorganic salts. The functionalized products of A-CTF-1 were dried in air.

Synthesis of the composite A-CNF

As shown in Scheme S1, a certain amount of CN nanosheets and the above-obtained A-CTF-1 powder were placed into quartz tube in a vacuum. 2.0 mL ethanol, 0.4 mL acetic acid and 2 mL 1,3,5-trimethylbenzene (Mesitylene, AR, 97%) were added into the above tube, and stirred at 25 °C for 3 day. The solution was centrifuged and subsequently washed several times with anhydrous tetrahydrofuran (THF, $\geq 99.9\%$), anhydrous acetone, and trichloromethane, respectively. The final powder of the A-CNF was dried at 120 °C for 12 h under vacuum.

Characterizations

The crystal phase was measured by X-ray diffraction (XRD, Bruker D8 CEVANCE) using graphite monochromatized Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The XRD data were collected by a scan mode with a scanning speed of 2°/min with 2 θ ranging from 5° to 80°. UV-vis diffuse reflectance spectra (DRS, Varian Cary 300) and photoluminescence spectra (F-7000, Hitachi, Japan) were used to analyze the optical properties of the as-prepared catalysts at room

temperature. Morphology and structure were studied with a field emission scanning electron microscope (SEM, Sirion 200, FEI, Holland) and a transmission electron microscope (TEM, Tecnai F20, FEI, USA). Fourier transformed infrared (FTIR) spectra of the samples were recorded by a VERTEX-70 spectrometer using KBr as reference. Brunauer-Emmett-Teller (BET) surface area of samples were measured by means of N₂ adsorption over a NOVA 2000e (Quantachrome) equipment. The element composition and valence state of catalysts was identified by X-ray photoelectron spectroscopy (XPS) (VG 250 Escalab spectrometer and Al-K = 1486.7 eV). Solid-state NMR spectra (crosspolarization magic-angle spinning (CP/MAS)) were carried out on a Bruker Avance 400 MHz spectrometer operating at 100.6 MHz for ¹³C.

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China), in the standard three-electrode cell system. There were platinum electrodes as counter electrode and standard calomel reference electrode in saturated KCl. The working electrodes were prepared by dip-coating: 10 mg of photocatalyst by supersonic extraction in 5 mL deionized water to produce a stable suspension that was then dip-coated onto a 4 cm × 1 cm fluorine-tin oxide (FTO) glass electrode, and the films were dried at room temperature. Na₂SO₄ (0.5 M) was used as electrolyte solution. As for photocurrent measurements, a 300 W Xe lamp (Perfect light PLS-SXE300C) was used as the source of simulated solar irradiation and the other conditions were the same as those of electrochemical measurements. Electrochemical Impedance Spectroscopy (EIS) was carried out in Na₂SO₄/K₃(Fe(CN)₆)/K₄(Fe(CN)₆) (Na₂SO₄ 0.5 M, K₃(Fe(CN)₆) 0.25 mM and K₄(Fe (CN)₆) 0.25 mM) solution over the frequency ranging from 0.01 Hz to 100 kHz at 0.24 V, and the amplitude of the applied sine wave potential in each case was 5 mV.

Test of photocatalytic activity

The experiments of photocatalytic H₂ evolution were carried out using a Pyrex top-irradiation reaction vessel connected to a glass closed gas system (Perfect Light, Beijing, Labsolar-III(AG) in a Pyrex flask). A 300 W Xe lamp (Perfect light PLS-SXE300C; Wavelength range: 420 nm ≤ λ ≤ 780 nm, light intensity: 160 mW/cm²) was used as the visible light source. The as-prepared catalyst (20 mg) was uniformly dispersed in 80 mL of aqueous solution

(containing H₂O/triethanolamine, v/v = 72:8). Then 3% Pt nanoparticles were deposited on photocatalysts as cocatalysts, which were rooted in H₂PtCl₆ by a photodeposition method. The system was vacuum-treated several times to remove the dissolved air. The amount of produced hydrogen was analyzed by an online gas chromatograph (GC7900). Meanwhile, the cooling water was used to maintain the temperature at about 6 °C. In order to ensure the reliability of the experimental results, the experiments of photocatalytic hydrogen evolution were repeated three times and the final values shown in the text are the mean values of triplicate results.

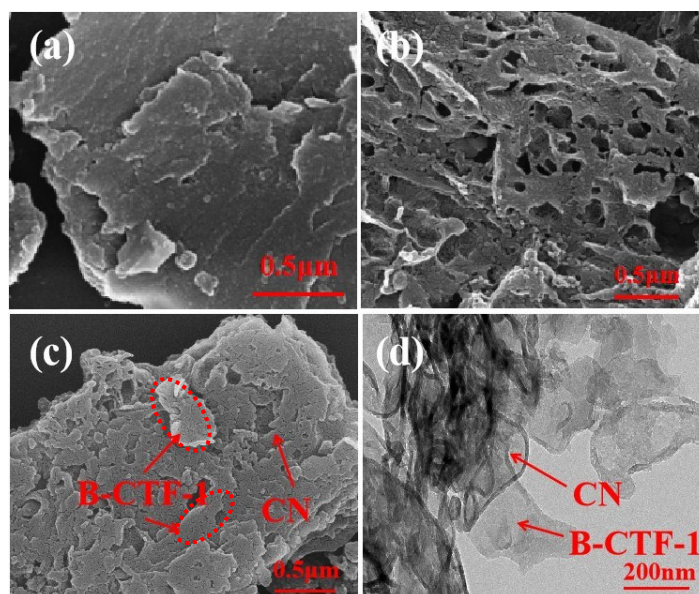


Figure S1. SEM images of (a) B-CTF-1, (b) CN and (c) 10CNF; (d) TEM image of 10CNF.

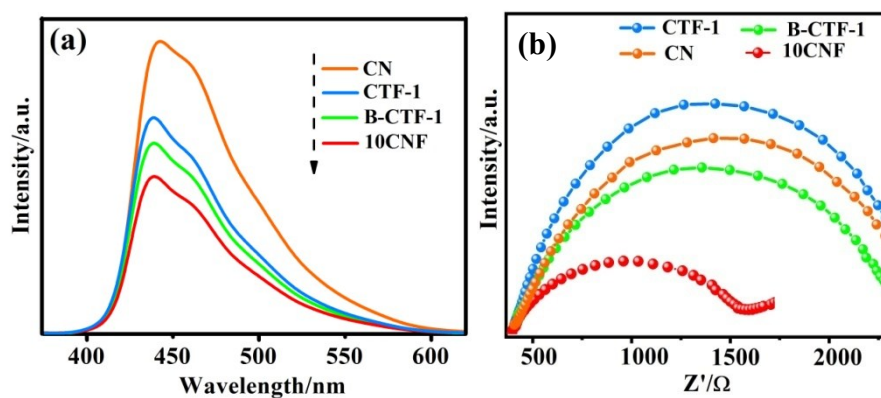


Figure S2. (a) PL spectra and (b) electrochemical impedance spectra of the as-prepared catalysts.

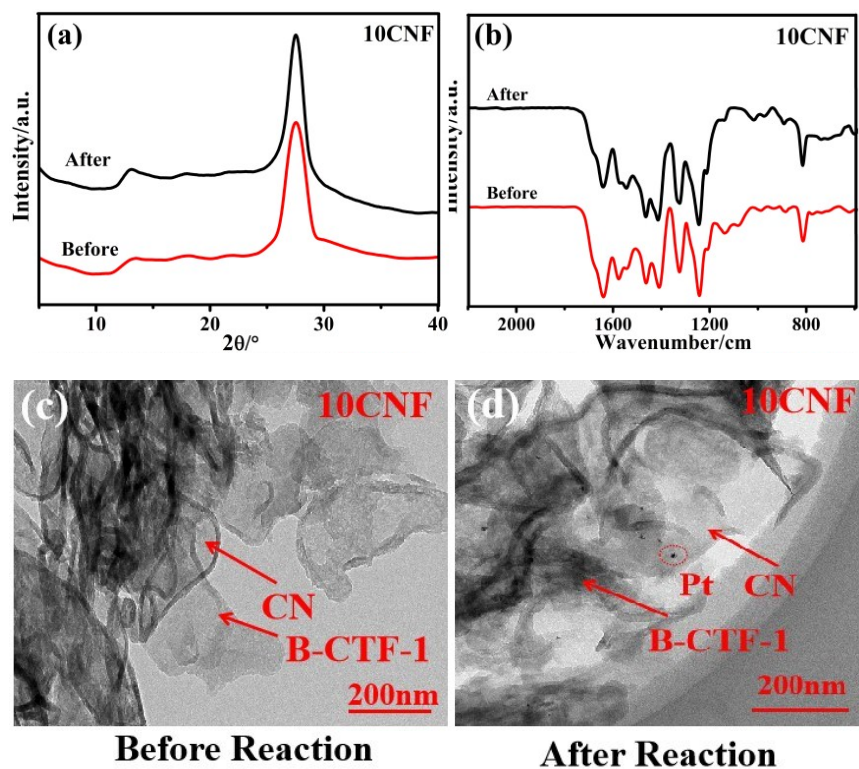


Figure S3. (a) XRD, (b) FTIR and (c and d) TEM images of the 10CNF before and after the photocatalytic reaction of 16 h.

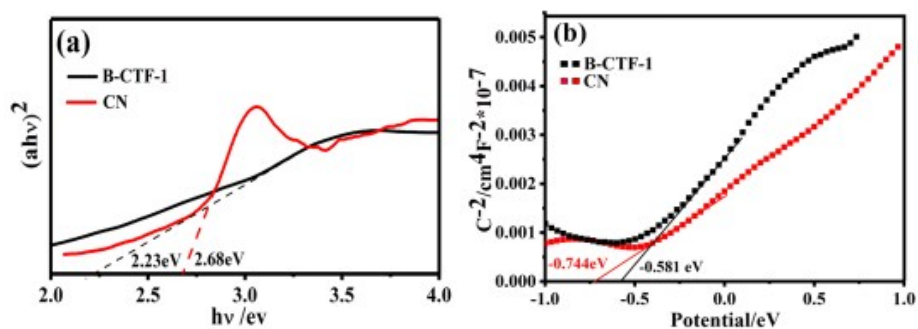


Figure S4. (a) The plots of transformed Kubelka-Munk function versus the light energy for as-prepared B-CTF-1 and CN; (b) Mott-Schottky plots of the CN and B-CTF-1.

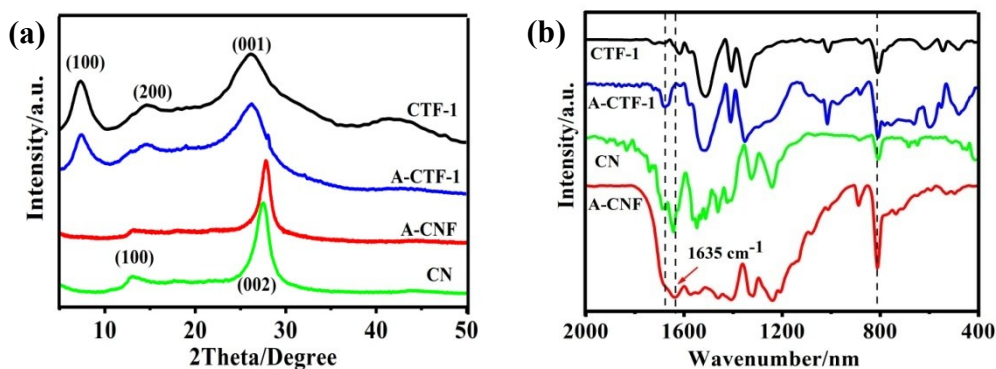


Figure S5. (a) XRD patterns and (b) FTIR spectra of the as-prepared catalysts of CN, CTF-1, A-CTF-1, and A-CNF.

As shown in **Figure S5a**, three diffraction peaks at 7.5° , 14.6° and 25.5° in CTF-1 and A-CTF-1, correspond to the crystal facets of (1 0 0), (2 0 0) and (0 0 1), respectively. The result suggests that the modification of aldehydes does not destroy the crystal structure of CTF-1. The A-CNF has similar peaks to the CN, and the characteristic peaks of A-CTF-1 cannot show in the XRD spectrum of the CNF when few doping amount of A-CTF-1. The phenomena could be explained that CN has much stronger diffraction peaks than A-CTF-1. And the shift of (0 0 2) peak indicates that A-CTF-1 could be interconnected with CN by covalent bonds via polar imine functional in the composite A-CNF.

Figure S5b shows the FTIR spectra of the as-prepared catalysts. All of the samples have a marked absorption peak of 813 cm^{-1} attributed to the vibration of s-triazine ring, indicating that the samples have the same structure (s-triazine ring). The spectrum of A-CTF-1 has a characterized fingerprint of C=O stretch at 1676 cm^{-1} , confirming that CTF-1 was successfully covalent-functionalized by 4-Iodobenzaldehyde. For the A-CNF, a new C=N stretching peaks at 1635 cm^{-1} was formed, whereas the C=O bonds disappeared, indicating that the imine bonds were formed between the CN and A-CTF-1.

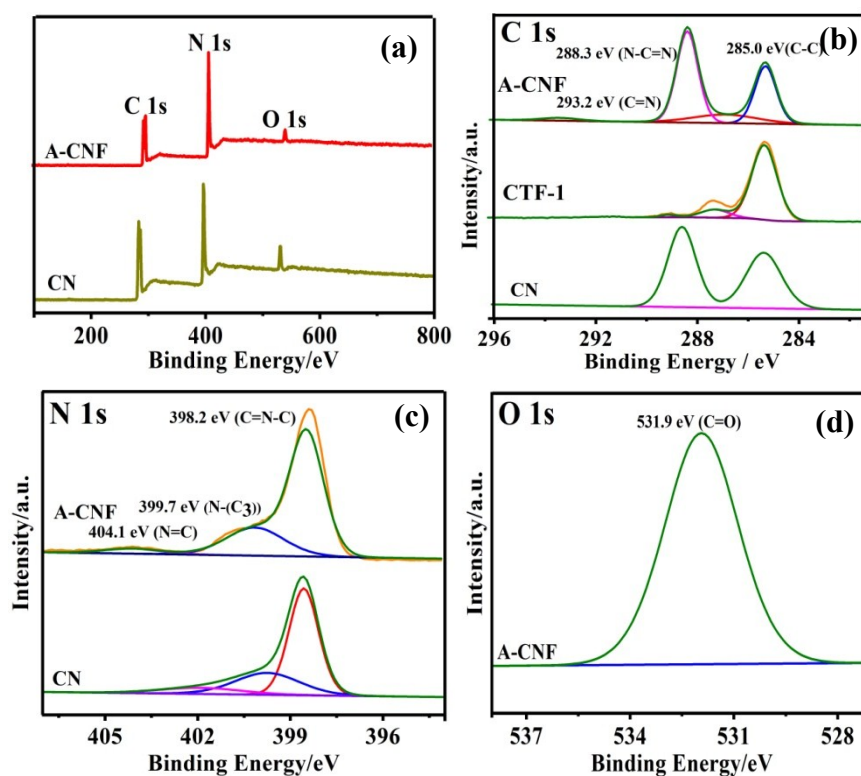


Figure S6. High-resolution XPS of spectra of (a) C 1 s and (b) N 1 s, (c) O 1 s and (d) XPS survey spectra of the CN, CTF-1 and A-CNF.

As shown in **Figure S6a**, The spectra of CN and A-CNF contain three peaks of C, N and O at 284.7, 398.8 and 532.3 eV, respectively, indicating the existence of C, N and O in the A-CNF. **Figure S6b** shows the C 1s spectrum of CN, CTF-1 and A-CNF. For the CN, two peaks at 285.0 and 288.3 eV can be attributed to the C-C and N-C=N groups of g-C₃N₄, respectively. For the CTF-1, the peaks at 285.0 and 286.2 eV can be ascribed to aromatic sp² carbon(C-C) and triazine carbon (C-N), respectively. Compare with the CN and CTF-1, the A-CNF has a new peaks in 293.2 eV, which could be attribute to the formation of imide (-C=N-). The N 1s spectrum of the A-CNF in **Figure S6c** has three peaks at 398.2, 399.7 and 401.7 eV, which can be ascribed to C=N-C, N-(C)₃ and C-NH_x groups, respectively. Noteworthy, the peak at 399.7 eV in the A-CNF has much higher intensities than that pure CN, illustrating that CN was coupled with A-CTF-1 by covalent bond. As shown in **Figure S6d**, a peak at 531.9 eV in the O 1s spectrum of the A-CNF can be ascribed to the C=O groups in aldehyde groups.

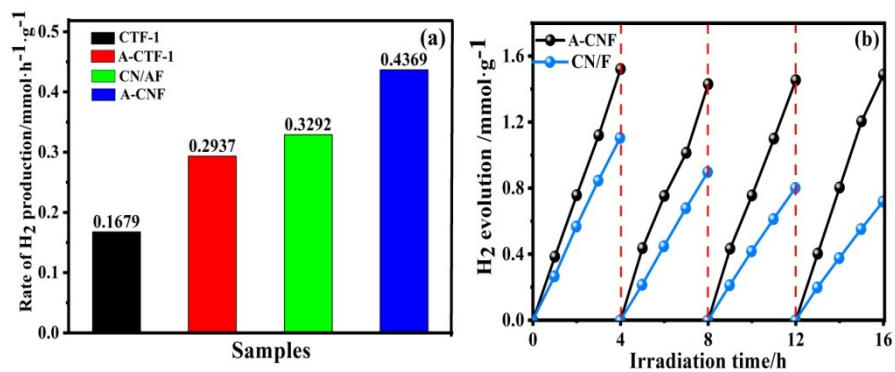
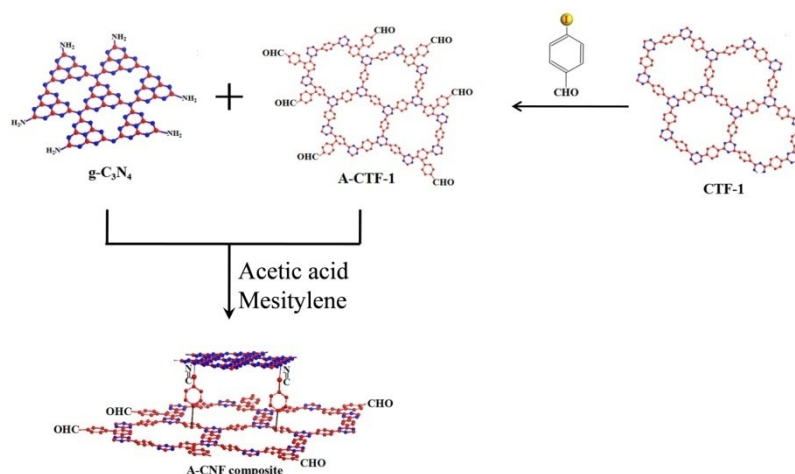


Figure S7. (a) H₂ evolution rate of the different samples under visible light irradiation; (b) H₂ evolution rate of the CN/F and A-CNF under visible light irradiation for four consecutive runs.



Scheme S1. Schematic representation of the synthesis of A-CNF composite.