**Electronic Supplementary Information**

# Towards efficient solar hydrogen production by intercalated carbon nitride photocatalyst

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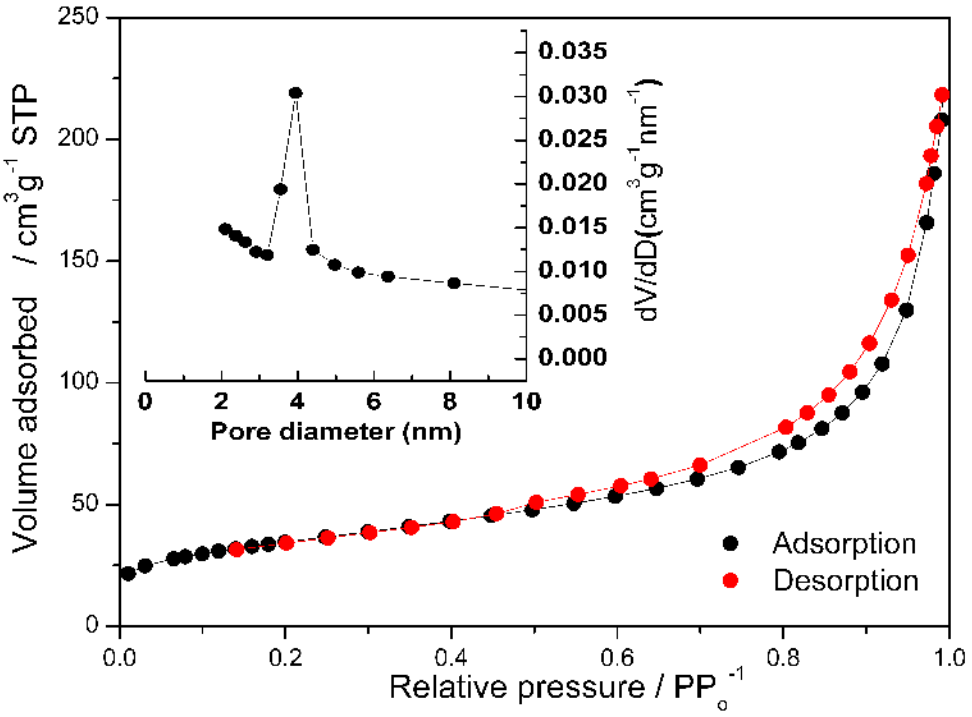
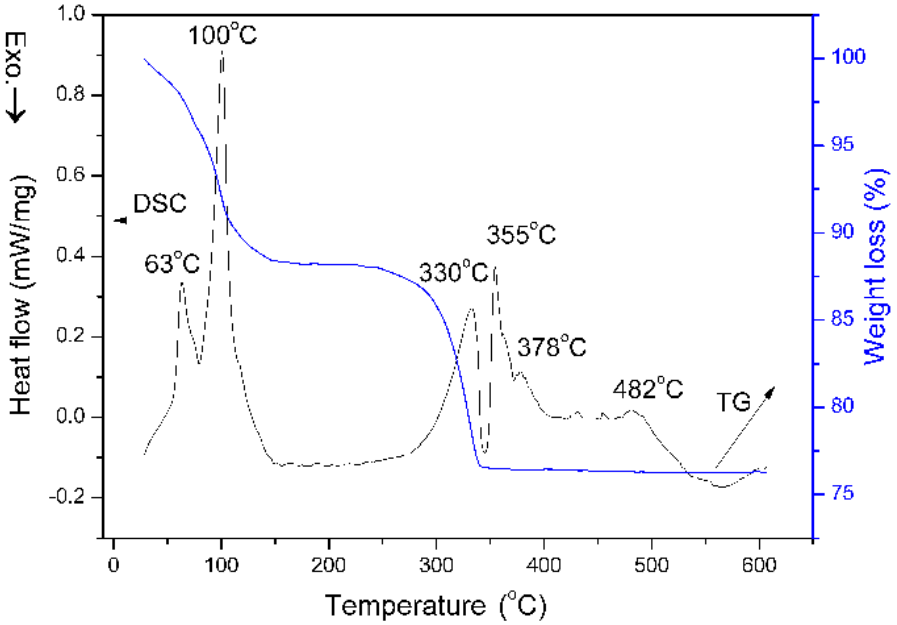
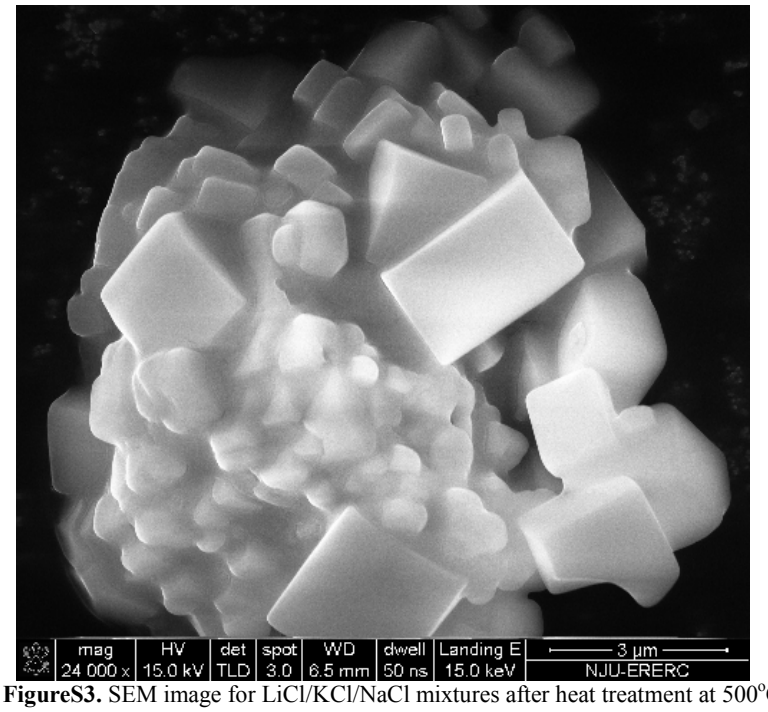



**Figure S1.** Nitrogen adsorption-desorption isotherms and pore size distribution (inset) for CNIC. The pore diameter calculated from the nitrogen adsorption isotherm by the Barrett-Joyner-Halenda (BJH) method is 4.0 nm, and the specific surface area calculated from the linear region of the Brunauer-Emmett-Teller (BET) plot ranging from $P/P_0$=0.05 to $P/P_0$=0.15 is 124$m^2$ $g^-$.




| T (°C) | Related process |
|---|---|
| 65 | Desorption of the water absorbed on the surface of mixing salts of NaCl, KCl and LiCl |
| 100 | LiCl • $H_2O$ loses all water of crystallization |
| 330 | Sublimation and condensation of melamine |
| 355 | Melting point of eutectic salts |
| 378 | Formation of polymeric melem |
| 482 | Formation of carbon nitride |

**FigureS2.** TG-DSC thermograms for heating melamine/ LiCl/KCl/NaCl mixtures with heating rate of 10°C/min.




**FigureS3.** SEM image for LiCl/KCl/NaCl mixtures after heat treatment at 500°C for 2h.

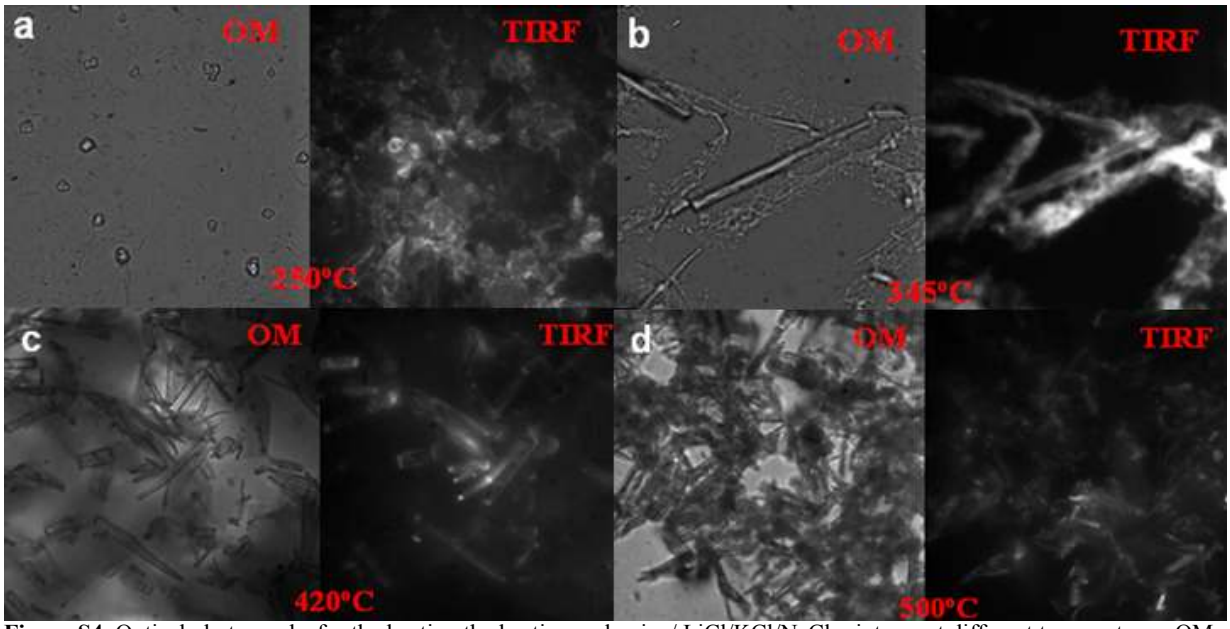



**Figure S4.** Optical photographs for the heating the heating melamine/ LiCl/KCl/NaCl mixtures at different temperatures. OM and TIRF indicate the optical imaging model and total internal reflection fluorescence imaging model, respectively.

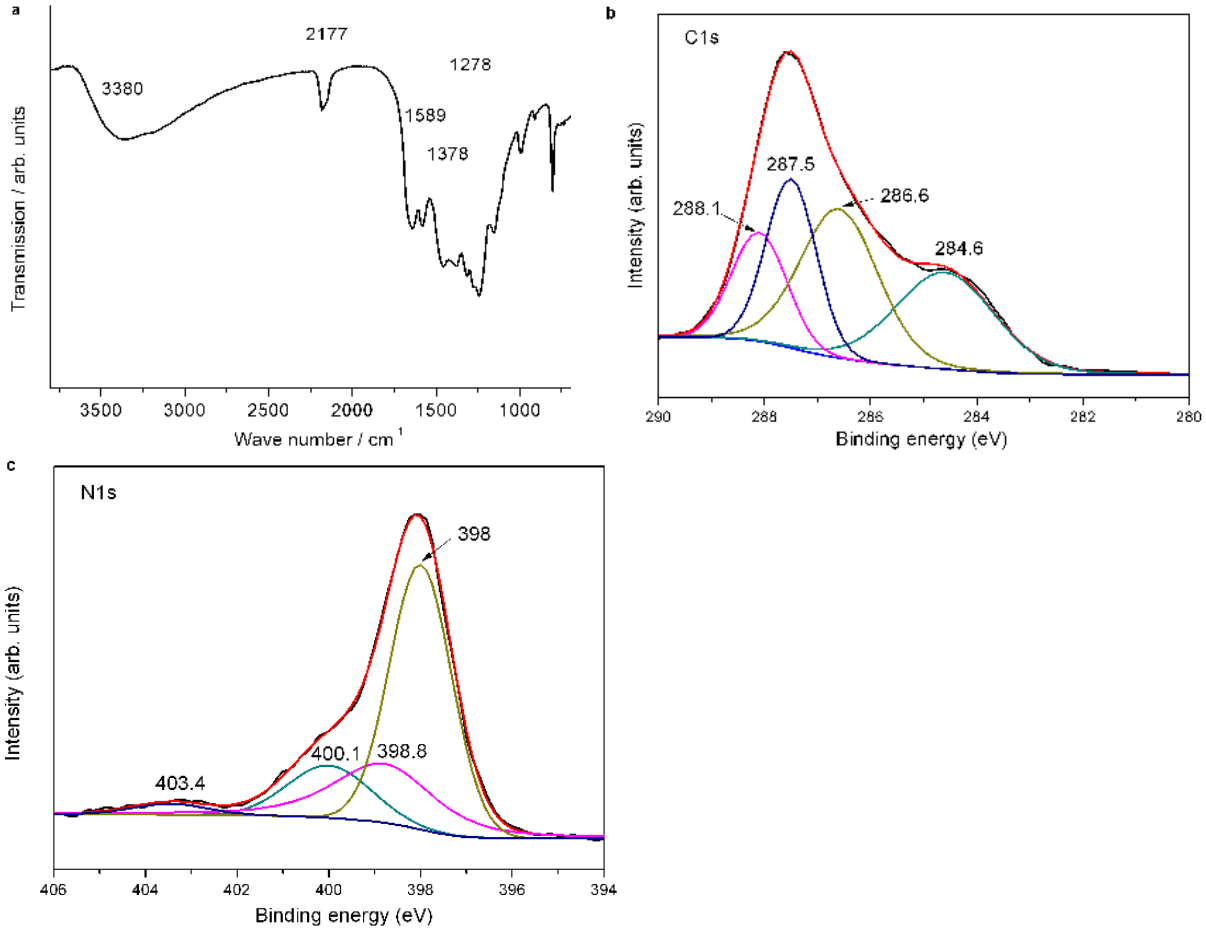



**Figure S5.** a) FTIR profile of CNIC. b) C1s and c) N1s XPS spectra of as-prepared CNIC.

The C1s peak (FigureS5b) for CNIC deconvolves into four components at binding energies of 284.6, 286.6, 287.5, and 288.1 eV, which are attributed to the C-C, C≡N, C-N and C= N bonds, respectively. The deconvoluted N1s peak (FigureS5c) shows a major component at 398 eV due to nitrogen $sp^2$-bonded to carbon, 398.8 C= N bond, a shoulder peak at a higher

binding energy, 400.1 eV, assigned to sp bonded nitrogen in the terminal C≡N groups, The peak at 403.4eV is attributed to the charging effects.

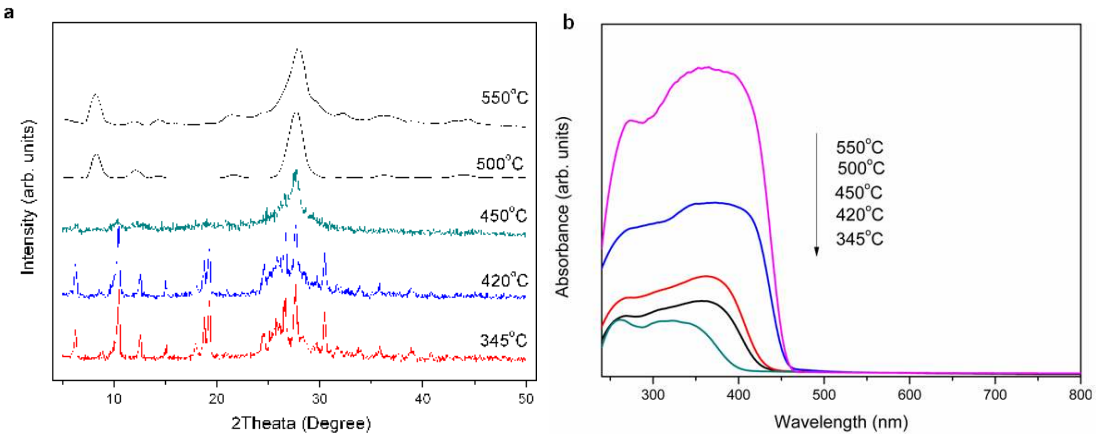



**Figure S6.** XRD patterns (a) and ultraviolet – visible diffuse reflectance spectra (b) for the products by heating melamine/ LiCl/KCl/NaCl mixtures at different temperatures.

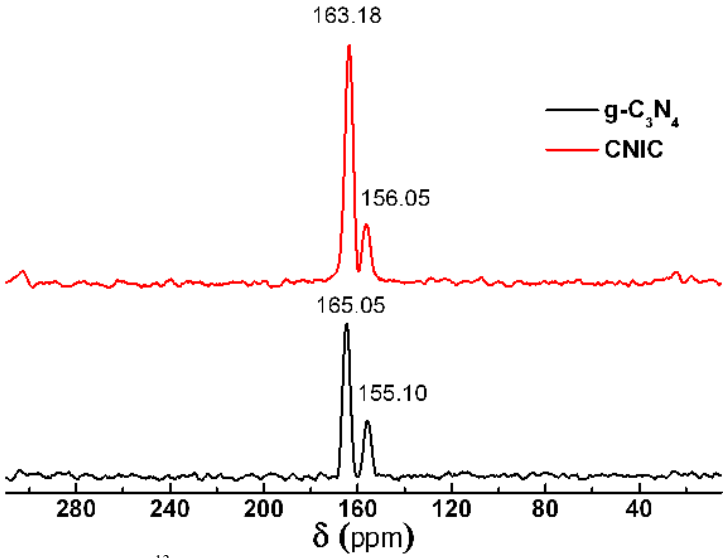



**Figure S7.** $^{13}C$ MAS NMR spectra of CNIC and g-$C_3N_4$ powders.

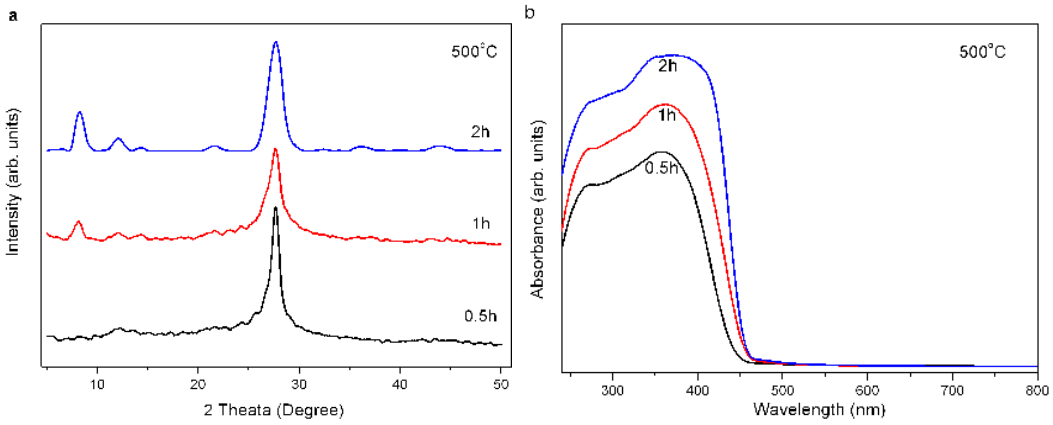



**Figure S8.** XRD patterns (a) and ultraviolet – visible diffuse reflectance spectra (b) for the products by heating melamine/LiCl/KCl/NaCl mixtures at 500°C for different reaction times.

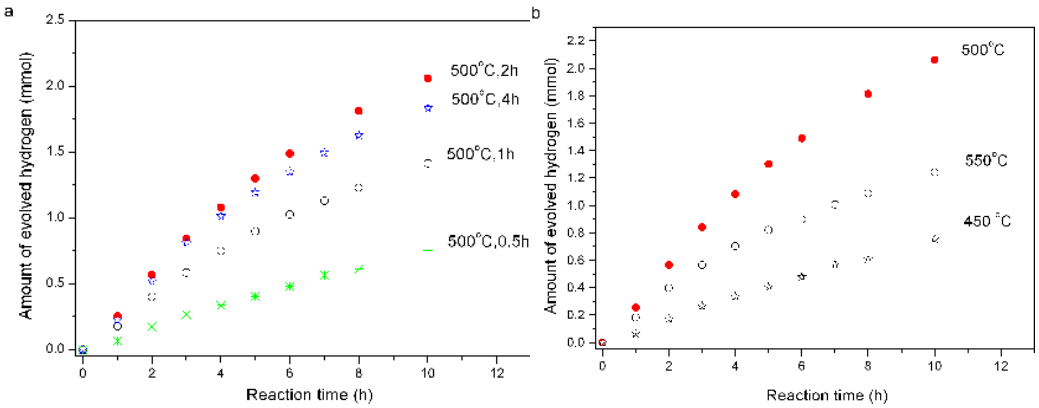



**Figure S9.** Hydrogen evolution from water over CNIC prepared under different conditions. a) CNIC prepared at 500°C for 0.5, 1, 2 and 4h. b) CNIC prepared at 450, 500 and 550°C for 2h. Visible light irradiation (of wavelength longer than 420 nm); 3.0 wt% Pt-deposited on surface of photocatalyst as cocatalyst and 10 vol% triethanolamine as sacrificial electron donor.

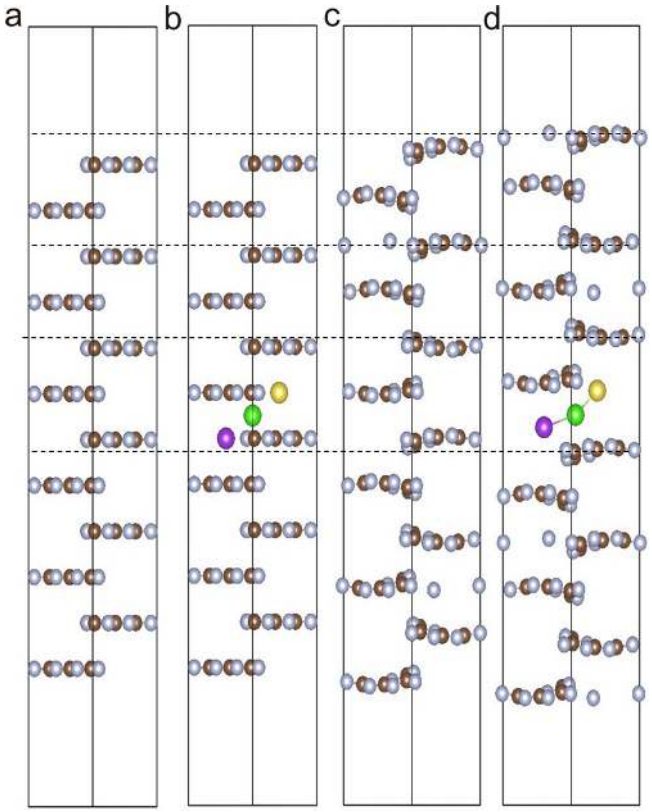



**Figure S10**. Structures of g-$C_3N_4$-(001) without (a) and with (c) relaxation. Structures of CNIC-(001)+(Cl, Na, K) without (b) and with (d) relaxation.

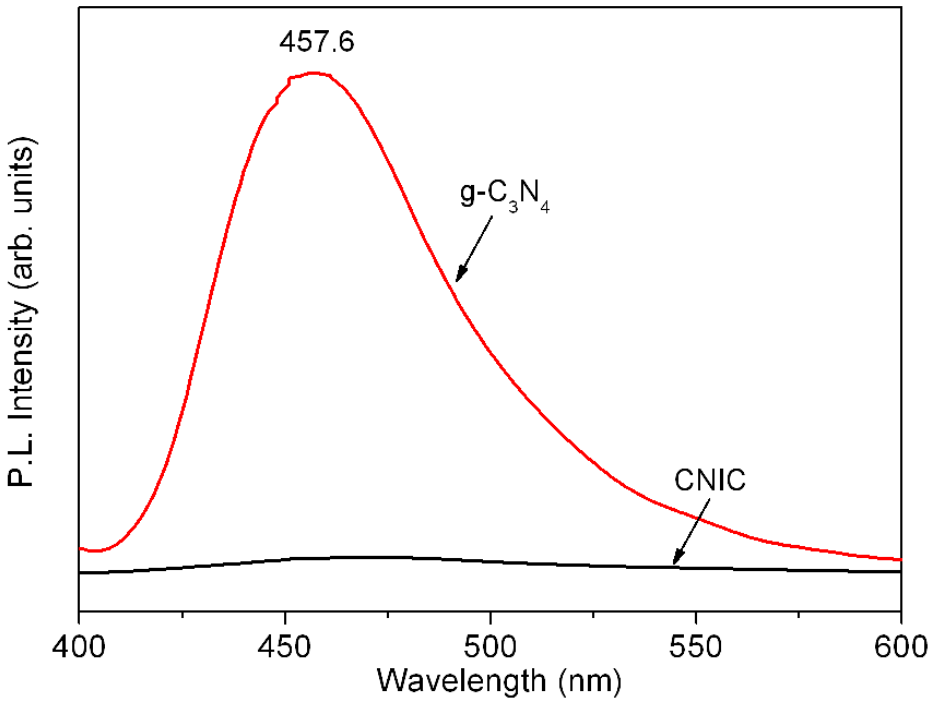



**Figure S11**. Photoluminescence (PL) spectra for CNIC and g-$C_3N_4$ with excitation wavelength at 350 nm.

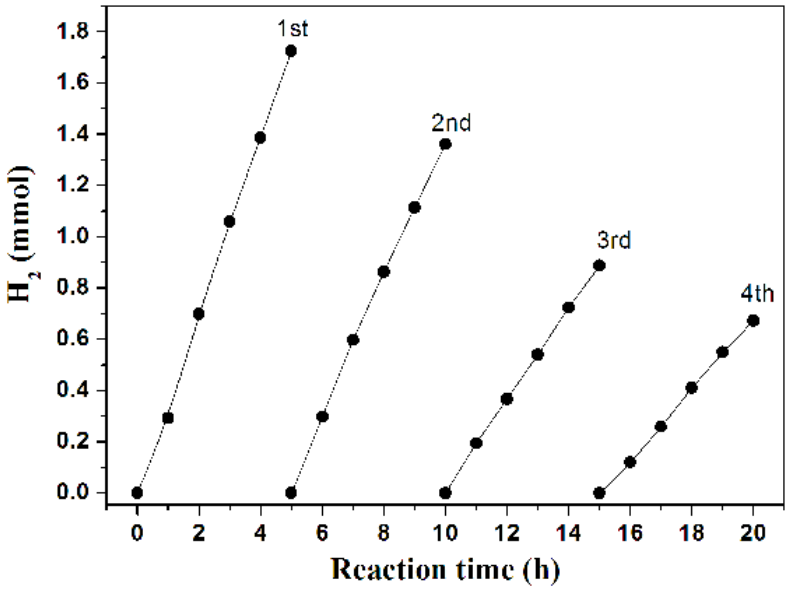



**Figure S12**. A typical time course of $H_2$ production from water containing 10 vol% triethanolamine as an electron donor under visible light (of wavelength longer than 420 nm) by 3.0 wt% Pt-deposited g-$C_3N_4$ photocatalyst. The reaction was continued for 20 h, with evacuation every 5 h.

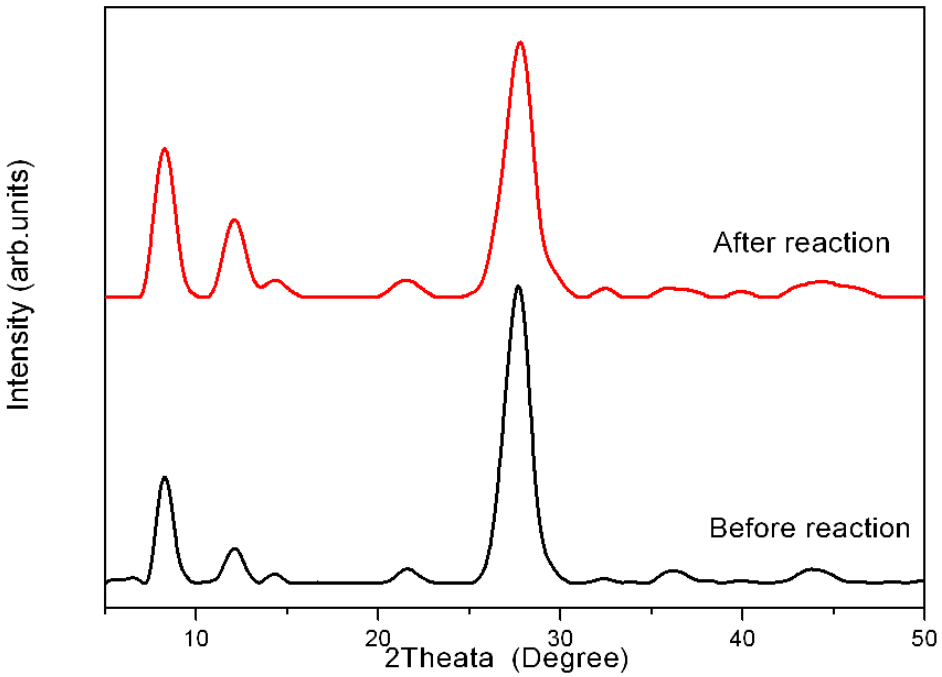



**Figure S13.** XRD patterns for the CNIC before and after reaction

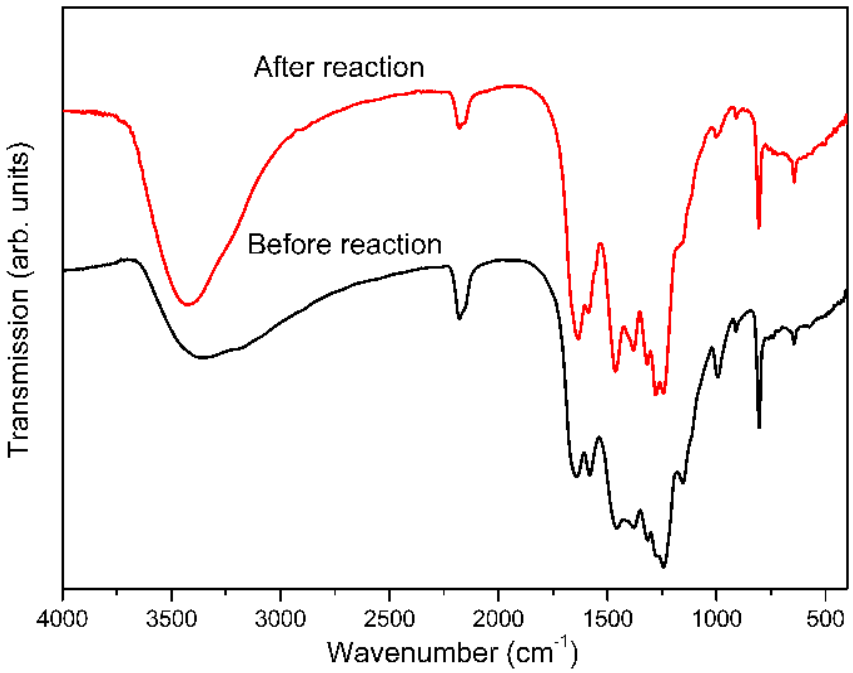



**Figure S14.** FTIR spectra for the CNIC before and after reaction

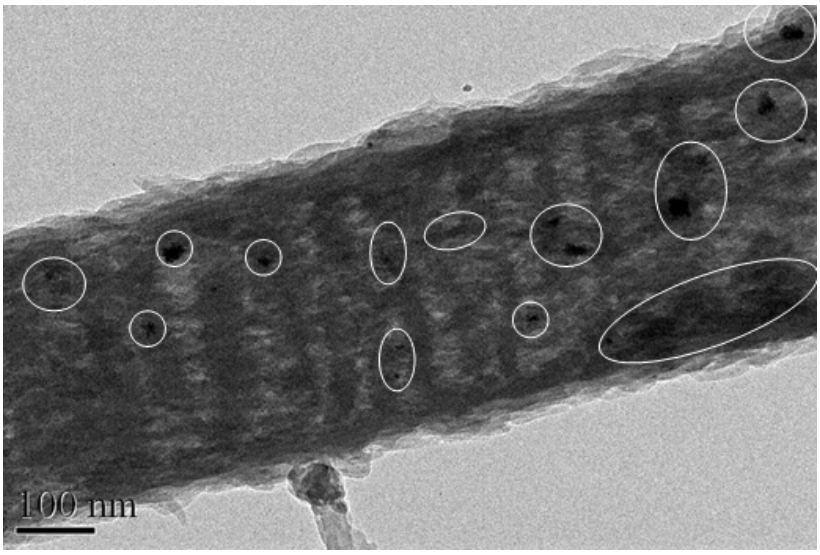



**Figure S15.** TEM image of CNIC after photocatalytic reaction. ○ indicates the Pt particles.

**Table S1.** Formation energies of CNIC-(001)+(Cl), CNIC-(001)+(Na, K) and CNIC-(001)+(Cl, Na, K) slab models.

| Slab models | Formation energies (eV) |
|---|---|
| CNIC-(001)+(Cl) | 1.20 |
| CNIC-(001)+(Na, K) | -3.09 |
| CNIC-(001)+(Cl, Na, K) | -5.74 |

**Table S2**. The atomic ratios for the CNIC before and after reaction

| | Atomic ratios | | | | |
|---|---|---|---|---|---|
| | N/C | Li/C | Na/C | K/C | Cl/C |
| Before reaction | 1.5 | 0.085 | 0.038 | 0.107 | 0.025 |
| After reaction | 1.43 | 0.065 | 0.019 | 0.088 | 0.013 |