

Electronic Supplementary Information

## Deprotonation of g-C<sub>3</sub>N<sub>4</sub> with Na ions for efficient nonsacrificial water splitting under visible light

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### Experimental Section

#### 1. Materials

Melamine (+99 %), *o*-tolidine (98 %), Nafion (D-520, 5 vol.%) and chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ≥ 37.5 % Pt basis) were purchased from Alfa Aesar. Sodium chloride (99.5 %), sodium sulfate (99 %), silver nitrate (99.99 %), triethanolamine (+99.5 %), N,N-dimethylformamide (+99.9 %) and hydrogen peroxide (30 vol.%) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the reagents were used as received without further purification.

#### 2. Synthesis of g-C<sub>3</sub>N<sub>4</sub> and deprotonated g-C<sub>3</sub>N<sub>4</sub>

Pure g-C<sub>3</sub>N<sub>4</sub> was prepared by heating 2 g melamine at 823 K for 4 h under flowing argon gas (99.99%, 50 mL min<sup>-1</sup>) with a ramp rate of 2 °C min<sup>-1</sup>, followed by naturally cooling to room temperature under argon gas. A light-yellow powder of g-C<sub>3</sub>N<sub>4</sub> was finally obtained with a yield of about 0.834 g. A typical synthesis of deprotonated g-C<sub>3</sub>N<sub>4</sub> is shown as follows: 1 g melamine mixed with 10 g sodium chloride was ground in planetary ball mill (QM-3SP04, Nanjing University Instrument Co.) at 400 rpm for 48 h. Then, the mixture was pressed into small

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tablets in order to ensure the interactions between the precursors in the thermal treatment. The tablets were transferred into a quartz tube and heated by the thermal processes identical to the pure g-C<sub>3</sub>N<sub>4</sub>. A bright-yellow powder of Na-CN was finally obtained with a yield of about 0.629 g. The resultant was ground and washed with deionized water by several cycles of centrifugal separation/washing/redispersion until the chloride ion concentration in the filtrate is negligible, checked by AgNO<sub>3</sub> test. The product (denoted as Na-CN) was then dried at 383 K for 12 h and finally kept in a darkened vacuum desiccator. The other deprotonated catalysts prepared by the melamine/sodium chloride in the weight ratios of 1 : 5, 2 : 15 and 2 : 25 were denoted as Na-CN-1, Na-CN-2, and Na-CN-3, respectively.

### 3. Characterization

X-ray powder diffraction (XRD) measurements were carried out with Cu *K*α radiation ( $\lambda = 1.5418$  Å) on a Rigaku D/MAX-RB diffractometer. Transmission electron microscopy (TEM) images were acquired using a FEI Tecnai G2 T20. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific Inc.) at  $3.0 \times 10^{-10}$  mbar with monochromatic Al *K*α radiation ( $E = 1486.2$  eV). All binding energies were referenced to the C 1s peak (284.6 eV) arising from the adventitious carbon. The Brunauer–Emmett–Teller (BET) surface area was determined by N<sub>2</sub> adsorption measurement using a Quantochrome autosorb iQ instrument at 77 K. All the samples were degassed at 473 K for 3 h before the measurement. UV-vis diffuse reflectance spectra (DRS) were measured on an UV-vis spectrometer equipped with an integrating sphere diffuse reflectance accessory (Shimadzu 2550). Photoluminescence spectroscopy (PL) was conducted by an Edinburgh FLS-920 spectrometer at room temperature.

### 4. Electrochemical measurement

Measurements were performed on an electrochemical analyzer (CHI660E Instruments) with a standard three-electrode cell using a Ag/AgCl electrode (3 M KCl) and a Pt plate as reference electrode and counter electrode, respectively. The electrolyte was 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH=7) and was purged with nitrogen gas for 2 h prior to the measurements. The pulse visible light was generated by a CEL-HXF 300 W xenon lamp with a 420 nm cut-off filter and chopped with an optical chopper (Stanford SR540). The working electrode was prepared as follows: 50 mg of sample was dissolved in 5 mL N,N-dimethylformamide (DMF) under sonication for 1 h to get a slurry. The slurry was cautiously spread onto glassy carbon electrode (diameter 5 mm), and was irradiated by IR light for 3 h to evaporate the solvent and improve adhesion. Then, Nafion aqueous solution (0.05 %, 10 μL) was dropped onto the resulting electrode and air-dried for 1 h at ambient temperature. The coated area of the electrode was about 0.20 cm<sup>2</sup>.

## **5. Photocatalytic test**

Photocatalytic H<sub>2</sub> and O<sub>2</sub> production was performed in a Pyrex top-irradiation vessel connected to a glass-closed gas circulation and evacuation system. The specific procedure was as follows: 100 mg well-ground catalyst powder was dispersed in an aqueous solution (100 mL) containing a small amount of H<sub>2</sub>PtCl<sub>6</sub> as the co-catalyst. In the case of deposition of Pt, the loading of 1.0 wt.% Pt cocatalyst on sample was performed by an in-situ photodeposition method. Before photocatalytic experiments, the reactant solution was evacuated for 30 min to ensure the anaerobic conditions. The CEL-HXF 300 W xenon lamp with a 420 nm cutoff filter was used again as the light source. A flow of cooling water was used to maintain the temperature of the reactant solution at 278 K. The evolved gases were analyzed by an online 7890 II gas chromatography equipped with a thermal conductive detector (TCD, argon as the carrier gas).

## **6. Quantum efficiency (QE) and solar to hydrogen (STH) conversion efficiency calculations**

## 6.1 Quantum efficiency calculation

The calculation of apparent quantum yield (AQY) was determined by using the following formula:

$$\text{AQY} = (2 \times \text{the number of evolved H}_2 \text{ molecules} / \text{the number of incident photons}) \times 100\%$$

In a typical measurement, a CEL-HXF 300 W Xe lamp with a band-pass filter ( $420 \pm 15$  nm) and an emission area of  $25.5 \text{ cm}^2$  served as the light source. The integrated light intensity was  $5.9 \text{ mW cm}^{-2}$  tested by an FZ-A spectroradiometer. The number of incident photons was calculated to be  $1.14 \times 10^{21}$ , using the following equation:

$$N = E \lambda / h c = (5.9 \times 10^{-3} \times 25.5 \times 3600 \times 420 \times 10^{-9}) / (6.626 \times 10^{-34} \times 3.0 \times 10^8) = 1.14 \times 10^{21}$$

The average  $\text{H}_2$  evolution rate on the deprotonated g- $\text{C}_3\text{N}_4$  was  $13.7 \mu\text{mol h}^{-1}$ , determined after 5h photocatalytic test without an additional sacrificial reagent. Therefore, the AQY can be estimated as:

$$\text{AQY} = [(2 \times 6.02 \times 10^{23} \times 13.7 \times 10^{-6}) / 1.14 \times 10^{21}] \times 100\% = 1.45 \%$$

## 6.2 Solar to hydrogen (STH) conversion efficiency calculation

The calculation of STH conversion efficiency under simulated solar irradiation (AM 1.5G) was determined by using the following formula:

$$\text{STH} = E_W / E_{\text{Solar}}$$

The energy generated by nonsacrificial water splitting ( $E_W$ ) was 68 J, when  $285.5 \mu\text{mol H}_2$  was detected after 8h of photocatalytic reaction, using the following equation:

$$E_W = 285.5 \times 10^{-6} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} = 68$$

2.46 eV is the free energy of water splitting.

After 8 h of illumination, the total incident power over the  $25.5 \text{ cm}^2$  irradiation area was 0.83 W, so that the total input energy ( $E_{\text{Solar}}$ ) was  $2.39 \times 10^4$  J using the following equation:

$$E_{\text{Solar}} = 0.83 \times 8 \times 3600 = 2.39 \times 10^4$$

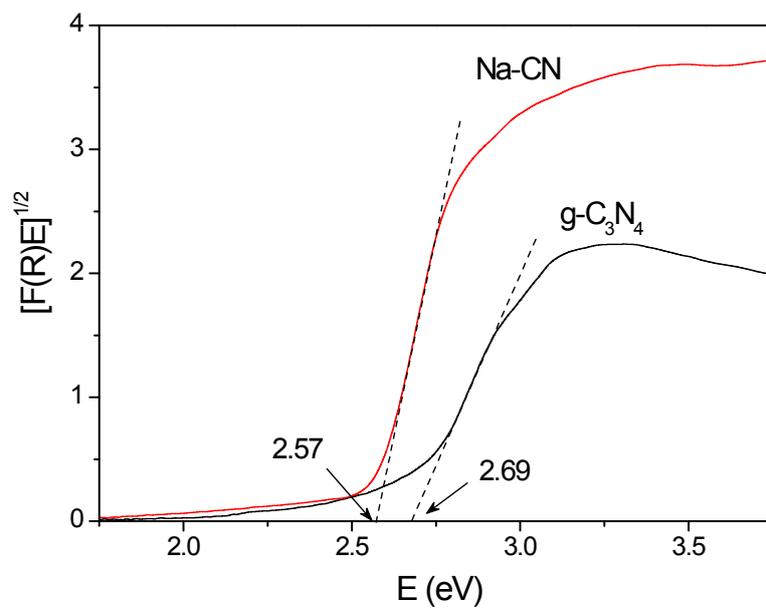
So the STH of Na-CN was determined to be:

$$\text{STH} = 68 / 2.39 \times 10^4 = 0.28 \%$$

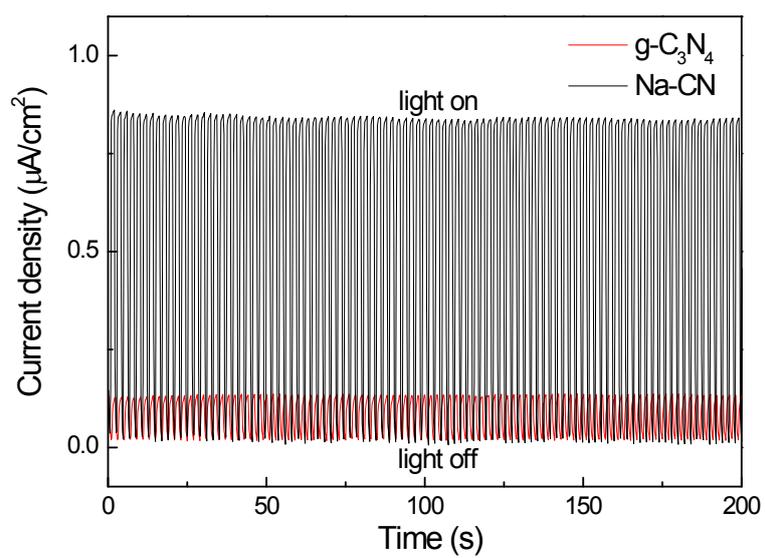
Similarly, the STH of g-C<sub>3</sub>N<sub>4</sub> was calculated to be 0.01 %, since 9.1 μmol H<sub>2</sub> was detected after 8h of nonsacrificial photocatalytic reaction.

## **7. H<sub>2</sub>O<sub>2</sub> detection**

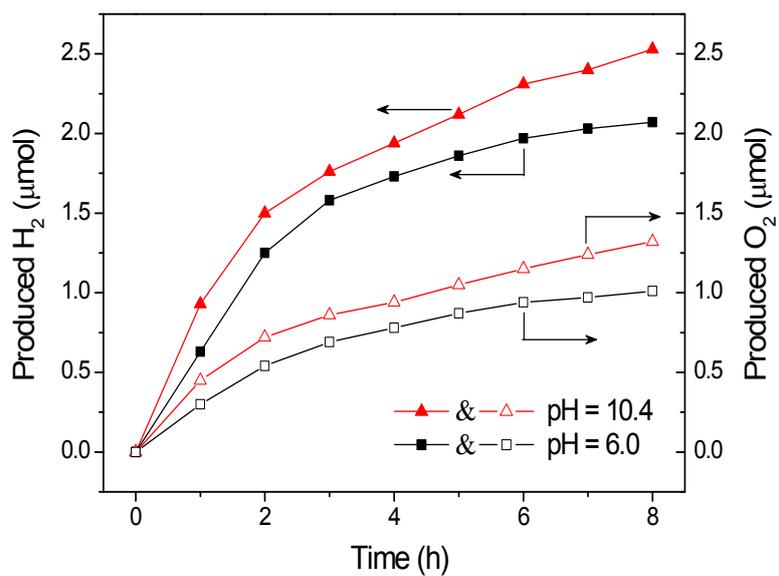
The concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in reaction solution was detected with a peroxide indicator, *o*-tolidine. Typically, 1.0 mL of reaction suspension was taken immediately after the reaction. The solution then centrifuged at 12000 rpm for 10 minutes to remove the catalyst. a 2.0 mL detection reagent of 1.0 % *o*-tolidine in 0.1M HCl was added to the centrifugal clear liquid to monitor the production of H<sub>2</sub>O<sub>2</sub> by measuring the absorption peak at 438 nm using UV-vis spectroscopy.



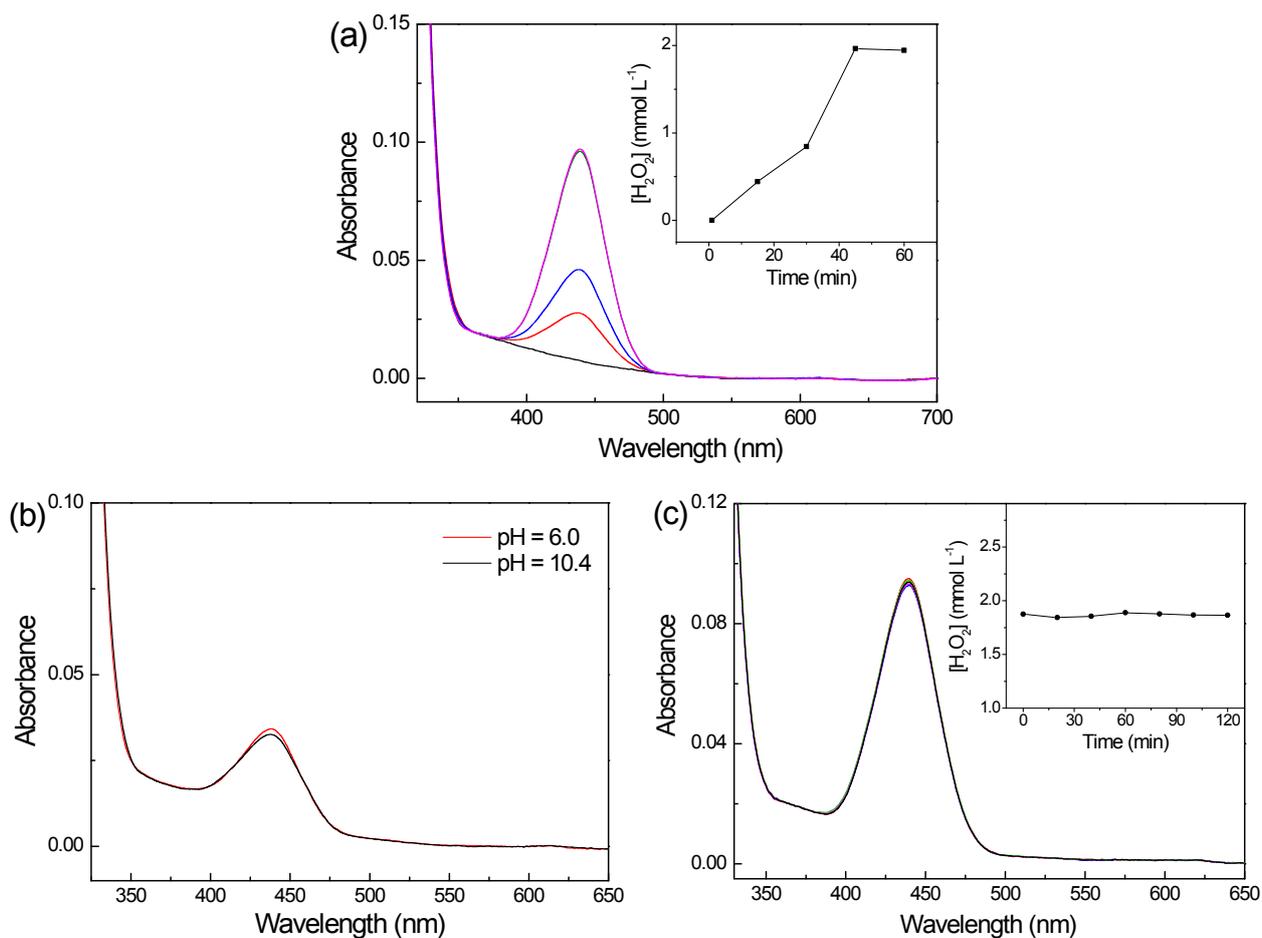
**Fig. S1** The data plotted as transformed K–M function versus energy of light absorbed.



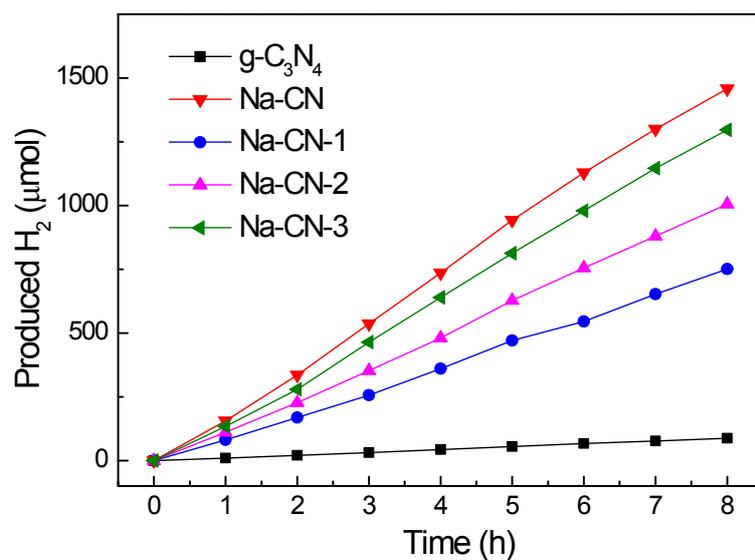
**Fig. S2** Transient photocurrent at 0.40 V (vs. RHE) under chopped illumination ( $\lambda > 420$  nm).



**Fig. S3** Photocatalytic nonsacrificial water splitting over 1.0 wt.% Pt-deposited g-C<sub>3</sub>N<sub>4</sub> at different pH under visible light irradiation ( $\lambda > 420$  nm).



**Fig. S4** (a) A time course of chromogenic reaction between  $\text{H}_2\text{O}_2$  ( $2 \text{ mmol L}^{-1}$ ,  $1.0 \text{ mL}$ ) and *o*-tolidine ( $1.0 \%$ ,  $2.0 \text{ mL}$ ) at ambient temperature. The absorption intensity at  $438 \text{ nm}$  reaches the maximum after  $45 \text{ min}$  reaction. So all the data for the following chromogenic reaction were collected after the mixing for  $45 \text{ min}$ . (b) Detection of  $\text{H}_2\text{O}_2$  in the nonsacrificial  $g\text{-C}_3\text{N}_4$  reaction suspension at different pH. (c) A time course of  $\text{H}_2\text{O}_2$  decomposition on  $1.0 \text{ wt.}\%$  Pt-deposited Na-CN under visible light irradiation ( $\lambda > 420 \text{ nm}$ ). In this experiment,  $1.0 \text{ mL}$   $\text{H}_2\text{O}_2$  ( $2 \text{ mmol L}^{-1}$ ) was added into the suspension ( $100 \text{ mg}$  catalyst dispersed in  $100 \text{ mL}$  aqueous solution), and was degassed like the aforementioned photocatalytic test.



**Fig. S5** Photocatalytic H<sub>2</sub> evolution over different catalysts deposited by 1.0 wt.% Pt in the presence of TEA under visible light irradiation ( $\lambda > 420$  nm). The average H<sub>2</sub>-evolution rates over g-C<sub>3</sub>N<sub>4</sub>, Na-CN, Na-CN-1, Na-CN-2 and Na-CN-3 are 10.5, 181.5, 93.8, 125.7 and 162.1  $\mu\text{mol h}^{-1}$ , respectively.

**Table S1.** XPS fitting data of the catalysts

Sample	C 1s				N 1s			
	Position	Assignment	FWHM	Area	Position	Assignment	FWHM	Area
g-C <sub>3</sub> N <sub>4</sub>	284.6	C-C	1.45	14035	398.6	C=N-C	1.27	162690
	286.3	C-NH <sub>x</sub>	1.05	3279	399.9	H-N-[C] <sub>3</sub>	1.53	54353
	288.1	C=N-C	1.23	106021	401.1	C-NH <sub>x</sub>	1.30	27911
Na-CN	284.6	C-C	1.49	22740	398.6	C=N-C	1.31	195525
	286.3	C-NH <sub>x</sub>	1.05	13035	399.9	H-N-[C] <sub>3</sub>	1.53	16111
	288.1	C=N-C	1.32	76971	401.1	C-NH <sub>x</sub>	1.29	15261

**Table S2.** XPS analysis of the catalysts

Sample	C 1s			N 1s		
	Position	Assignment	C/C <sub>total</sub> atomic ratio	Position	Assignment	N/N <sub>total</sub> atomic ratio
g-C <sub>3</sub> N <sub>4</sub>	284.6	C-C	–	398.6	C=N-C	0.664
	286.3	C-NH <sub>x</sub>	0.030	399.9	H-N-[C] <sub>3</sub>	0.222
	288.1	C=N-C	0.970	401.1	C-NH <sub>x</sub>	0.114
Na-CN	284.6	C-C	–	398.6	C=N-C	0.862
	286.3	C-NH <sub>x</sub>	0.145	399.9	H-N-[C] <sub>3</sub>	0.071
	288.1	C=N-C	0.855	401.1	C-NH <sub>x</sub>	0.067

**Table S3.** Result of the N<sub>2</sub> adsorption for the different catalysts

Sample	g-C <sub>3</sub> N <sub>4</sub>	Na-CN	Na-CN-1	Na-CN-2	Na-CN-3
S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	10.3	14.4	13.6	13.9	14.7