# **Supporting Information**

# Baking "crumbly" carbon nitrides with improved photocatalytic properties using ammonium chloride

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### Materials

Cyanamide (99 %), melamine (99%), and hexachloroplatinic acid ( $H_2PtCl_6$ ) solution (8 wt. % aqueous solution) were purchased from Sigma Aldrich, triethanolamine (TEOA, 98 %) was purchased from Alfa Aesar, and ammonium chloride (99.5%) was purchased from Fluka. All the chemicals were used without further purification.

## Typical procedure of g-CN synthesis using ammonium chloride as a template

A mixture of cyanamide and ammonium chloride was dissolved in minimal amount of deionized water. Water was evaporated under the reduced pressure, and the residue was dried at 50 °C in vacuum (10 mbar). The solid reaction mixture was transferred into a porcelain crucible, covered with a lid and placed in the oven. Alternatively, the solution of cyanamide and ammonium chlorde was directly transferred into a crucible (to obtain the the product abbreviated as 1:10-CA/NH<sub>4</sub>Cl-DH-CN), and heated up as follows. The reaction mixture was heated up in a heating oven with the ramp of 2.2 K·min<sup>-1</sup> from room temperature to 550 °C, maintained at 550 °C for 4 hours and then allowed to naturally cool down to room temperature. The synthesis was carried out under N<sub>2</sub> flow (50 L/min). The products were obtained as yellow powders; the yields are indicated in the Table S1.

In another experiment, 1.00 g of melamine was ground together with 10.0 g of ammonium chloride during 20 minutes in a mortar. The reaction mixture was then transferred into a porcelain crucible and heated up with the ramp of 2.2 K·min<sup>-1</sup> from room temperature to 550 °C, maintained at 550 °C for 4 hours and then allowed to naturally cool down to room temperature. The synthesis was carried out under N<sub>2</sub> flow (50 L/min). The product (1:10-Melamine/NH<sub>4</sub>Cl-CN) yield was 0.35 g.

The reference graphitic carbon nitride (ref.-CN) was obtained by heating melamine up to 550 °C, holding at this temperature for 4 hours, and then cooling down. The synthesis was carried out under N<sub>2</sub> flow (50 L/min). The final product was thoroughly ground using mortar and pestle during 30 minutes. The reaction mixture was transferred into a porcelain crucible and heated up in N<sub>2</sub> flow (50 L/min) with the ramp of 2.2 K·min<sup>-1</sup> from room temperature to 550 °C, maintained at 550 °C for 4 hours and then allowed to naturally cool down to room temperature.

#### The experiment aimed at recovery of the template

To demonstrate the possibility to recover the template, the reaction was carried out in a glass flask heated with a heating mantel, and the volatile reaction products were collected at the outlet of the reactor. Heating of the reaction mixture of 1.00 g cyanamide and 5.00 g of ammonium chloride to 550 °C was accompanied by the production of the white fumes followed by the condensation of some white and colorless products at the outlet of the reactor, in a temperature zone of 100 – 150 °C. The solid products were collected after the reaction, and analyzed by PXRD (see Fig. S1 below). The main product was found to be ammonium chloride, but the presence of some impurities was evident as well. In order to analyze the nature of the impurities and to purify the template, the mixture was poured with warm water. The precipitate was filtered and washed with warm deionized water (3x5 mL), while aqueous solution was evaporated under reduced pressure and dried in vacuum affording pure NH<sub>4</sub>Cl (4.91 g, 98%). It is possible that the missing 2% of the template can be explained by the presence of water in the used NH<sub>4</sub>Cl. The purity of the recovered template was confirmed by PXRD, by the identity of the patterns of the initial and the recovered NH<sub>4</sub>Cl (see Fig. S1 below). The precipitate collected by filtration was dried in vacuum affording 0.284g of a white solid. The EDS analysis showed that it is composed of C and N, with a weight ratio of 0.52 which is lower than the one for g-CN, and contains no chlorine. Moreover, upon subsequent heating at 550 °C for 4 hours this polymer could be converted into g-CN. Therefore, we concluded that the white solid represents some condensation intermediates, most probably heptazine-based oligomers. In principle, these oligomers can be recycled together with the template, thus increasing the yield of the final product and eliminating the need to purify the template.

The mass balance of the reaction using 1.00g of cyanamide and 5.00g of  $NH_4Cl$  is given in the Table S2.

#### Hydrogen evolution set up and measurement procedure

All catalytic experiments were carried out under argon atmosphere. The double walled and thermostatically controlled reaction vessel was connected to a digital pressure sensor (Type-P30, DP = 0.1%, WIKA Alexander Wiegand SE & Co. KG, Germany) to monitor the pressure increase due to hydrogen evolution. 25 mg of sample was placed inside the reactor; then the reactor was evacuated and refilled with argon for several times. Water and TEOA were pre-treated before

use. Water was first degassed for 1 h under vacuum in an ultrasonic bath followed by purging with argon for 1 h. TEOA was separately purged for 1 h with argon. The solvent mixture (total volume 38 mL) composed of water and triethanolamine (TEOA) in the ratio of 9/1 (v/v) and 19.7  $\mu$ L H<sub>2</sub>PtCl<sub>6</sub> solution (corresponds to theoretical Pt loading of 3 wt. % onto the catalyst), were added in the reactor. The temperature in the reactor was maintained at 25 °C by a thermostat. After stirring for 10 min to reach thermal equilibrium, the reaction was started by switching on 50 W white LED array (Bridgelux BXRA-50C5300,  $\lambda > 410$  nm) or 12 W blue LED array (Osa Opto Light, OLM-018 air,  $\lambda = 420$  nm). The amount of evolved gas was continuously monitored as time-dependent pressure increase. The hydrogen evolution rate was calculated according to the ideal gas law:

$$\dot{n} = \frac{n}{t} = 10^5 \frac{\Delta p \cdot V}{R \cdot T \cdot t}$$

where  $\dot{n}$  is hydrogen evolution rate [µmol/h], *n* moles hydrogen [µmol], *t* illumination time [h],  $\Delta p$  pressure increase [bar] during irradiation time *t*, V volume of the headspace above the reaction mixture, *R* universal gas constant [8.314 J/(mol·K)] and *T* temperature [298 K]. To confirm that the evolved gas is hydrogen, the headspace of the reactor was analyzed by GC-MS after the test. GC-MS analysis was performed using a Shimadzu GCMS-QP2010 equipped with a capillary column (HP-Plot/Q, 30 m, 0.25 mm, 20 µm). The measurement was running under isothermal conditions at 40 °C column temperature. Helium was used as a carrier gas; before injection of the headspace sample, the sample loop was purged with argon.

Characterization. Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with  $Cu_{K\alpha}$  radiation ( $\lambda = 0.15418$ nm) applying  $2\theta$  step size of 0.05° and counting time of 4s per step. FT-IR spectra were recorded on a Varian1000 FT-IR spectrometer equipped with an attenuated total reflection unit applying a resolution of 4 cm<sup>-1</sup>. Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 20 hours using a Quantachrome Quadrasorb SI-MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) model to adsorption isotherms for  $0.05 < p/p_0 < 0.3$  using the QuadraWin 5.05 software package. Elemental analysis (EA) was accomplished as combustion analysis using a Vario Micro device. Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope. Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere. The emission spectra were recorded on LS-50B, Perkin Elmer instrument. The excitation wavelength was 350 nm. Energy-dispersive X-ray spectroscopy (EDS) investigations were conducted on a JEOL JSM-7500F microscope using Link ISIS-300 system (Oxford Microanalysis Group) equipped with a Si(Li) detector with an energy resolution of 133 eV, at 5-12 keV. Zeta-potential measurements were performed using Zetasizer Nano ZS (Malvern), and the data analysis was conducted using Zetasizer software.

Product name	Precursor	Precursor amount, g	NH <sub>4</sub> Cl, g	g-CN, g
1:2-CA/NH <sub>4</sub> Cl-CN	cyanamide	1.50	3.0	0.61
1:5-CA/NH <sub>4</sub> Cl-CN	cyanamide	1.50	7.5	0.64
1:10-CA/NH <sub>4</sub> Cl-CN	cyanamide	1.50	15.0	0.45
1:10-CA/NH <sub>4</sub> Cl-DH-CN	cyanamide	1.00	10.0	0.37
1:10-Melamine/NH <sub>4</sub> Cl-CN	melamine	1.00	10.0	0.35
refCN melamine		1.00	-	0.34

Table S1. Amounts of the reagents and templates used for the synthesis.

Reaction mixture		Products		
Compound	Weight, g	Compound	Weight, g	
Cyanamide	1.00	g-CN	0.233	
NH <sub>4</sub> Cl	5.00	condensation oligomers	0.284	
		NH <sub>4</sub> Cl	4.91	

Table S2. Mass balance of the reaction aimed at recovery of the template.

Product	C, wt.%	N, wt.%	C/N	H, wt.%	0, wt.%
refCN	34.9	60.5	0.577	2.00	2.6
1:2-NH <sub>4</sub> Cl-CN	34.0	58.6	0.580	2.12	5.28
1:5-NH <sub>4</sub> Cl-CN	34.1	58.6	0.582	2.03	5.27
1:10-NH <sub>4</sub> Cl-CN	34.2	59.0	0.580	2.01	4.79
1:10-NH <sub>4</sub> Cl-DH*-CN	34.2	58.4	0.585	2.01	5.39

Table S3. Elemental composition of the products prepared at different cyanamide to ammonium chloride ratios, according to elemental analysis (C, N, H) and EDS (O) data. \*DH stands for "direct heating" of the aqueous reaction mixtures, without intermediate drying step.



Figure S1. PXRD patterns of the initial template (ammonium chloride), the template collected directly after the synthesis, and the washed template.



Figure S2. FTIR spectra of the reference bulk carbon nitride (ref.-CN) and ammonium chloride derived products.

a)





e)



**b)** 10:1-NH<sub>4</sub>CI-DH-C 1 μm

d)







Figure S3. SEM images of the products prepared at 1:2 (a, e, f, g), 1:5 (h, i) and 1:10 (b) cyanamide to  $NH_4Cl$  ratios, at 1:5 ratio using dicyandiamide as a precursor (c), and of reference ground carbon nitride, ref.-CN (d). \*DH stands for "direct heating" of the aqueous reaction mixtures, without intermediate drying step.



Figure S4.  $N_2$  sorption isotherms of the ref.-CN and  $NH_4Cl$ -derived products prepared using different CNpolymer precursors and mixing procedures with ammonium chloride, namely dissolution followed by the direct heating in the case of cyanamide and grinding in the case of melamine. \*DH stands for "direct heating" of the aqueous reaction mixtures.



Figure S5. PXRD patterns (a) and FTIR spectra (b) of the product prepared using 1:10 cyanamide to ammonium chloride weight ratio, before and after 17 hours of hydrogen evolution test.