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Improving Hydrogen Production for Carbon-Nitride-Based Materials: Crystallinity, Cyanimide Groups and Alkali Metals in Solution Working Synergistically

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1. Experimental

1.1 Synthesis of Na-PHI: Sodium poly(heptazine imide) (Na-PHI) was prepared by thermocondensating a mixture of melamine (10 g) with NaCl (100 g) previously grounded in a ball mill for 5 min. The reaction mixture in an alumina crucible (100 mL) was heated up in an oven under constant nitrogen flow (1 L min^{-1}) to 600 °C with a heating rate of 138 °C h^{-1}, held at 600 °C for 4 h, and then allowed to cool down. The product was removed from the crucible, washed with deionized water (1 L), isolated by centrifugation (9000 rpm, 5 min), and then thoroughly washed with deionized water on the filter (1 L). After that, it was dried overnight in a vacuum oven (10 mbar) at 60 °C.

1.2 Synthesis of K-PHI: Potassium poly(heptazine imide) (K-PHI) was prepared by thermocondensating a mixture of melamine (10 g) with KCl (100 g) previously grounded in a ball mill for 5 min. The reaction mixture in an alumina crucible (100 mL) was heated up in an oven under constant nitrogen flow (1 L min^{-1}) to 600 °C with a heating rate of 138 °C h^{-1}, held at 600 °C for 4 h, and then allowed to cool down. The product was removed from the crucible, washed with deionized water (1 L), isolated by centrifugation (9000 rpm, 5 min), and then thoroughly washed with deionized water on the filter (1 L). After that, it was dried overnight in a vacuum oven (10 mbar) at 60 °C.

1.3 Synthesis of NCN-K-PHI: NCN-K-PHI was prepared by adapting the method reported by Lotsch *et al.*[1] 10 g of the prepared K-PHI was grounded with 20 g of KSCN. The reaction mixture in an alumina crucible (100 mL) was heated up in an oven under constant nitrogen flow (1 L min^{-1}) to 400 °C for 1 h with a heating rate of 2.3 °C min^{-1}, and then heated to 500 °C held for 30 min and allowed to cool down. The product was removed from the crucible, washed with deionized water (1 L), isolated by centrifugation (9000 rpm, 5 min), and then thoroughly washed with deionized water on the filter (1 L). After that, it was dried overnight in a vacuum oven (10 mbar) at 60 °C.

1.4 Synthesis of LiK-PHI: LiK-PHI was prepared according to the synthesis method reported by Dontsova *et al*.[2] A mixture of 5-aminotetrazole (0.99 g) and LiCl/KCl eutectics (4.97 g 9:11 wt. ratio (2.24 g LiCl/ 2.73 g KCl)) was placed in a steel ball mill cup. The steel ball was inserted, and the cup was closed. The mixture of precursors was ground for 5 min at the operational frequency 25 Hz. The resultant flour-like white powder was transferred into a porcelain crucible, covered with a porcelain lid, and placed in an oven. The temperature inside the oven was increased from 20 to 600 °C within 4 h (2.4 K.min^{-1}) under a flow of nitrogen (15 L.min^{-1}), after which it was maintained at 600 °C for another 4 h. After that, the oven was allowed to cool slowly to room temperature. The melt from the crucible was transferred into a beaker, and deionized water (50 mL) and a stir bar were added. The suspension was stirred at room temperature for 4 h until it became homogeneous and no agglomerated particles were seen. The solid was separated by centrifugation (6500 min^{-1}, 12 min). The aqueous solution was carefully removed and the residue was transferred into a 50 mL tube. The solid was washed with water (3 × 10 mL) using a centrifuge (9000 rpm, 5 min) and dried in a vacuum oven (10 mbar) at 60 °C.

1.5 Synthesis of CN-OA-m: The synthesis for CN-OA-m was carried out using a slightly adapted version of the literature procedure [3]: 10 g of urea and 0.5 g of oxamide were mixed in 10 mL of deionized (DI) water to generate a homogeneous mixture. After drying at 100 °C, the resulting solids were ground and transferred into a crucible with a cover and heated up in an air-oven with a heating rate of 4.3 K.min^{-1} to 500 °C. After keeping the mixture for 2 h at 500 °C, the sample was allowed to cool to room temperature. After that KCl (3.3 g, 44.3 mmol) and LiCl (2.7 g, 63.7 mmol) were added and the solids were ground to obtain a homogeneous mixture which was heated in an inert atmosphere (N_2 flow: 1L.min^{-1}) to 600 °C with a heating rate of 4.6 K.min^{-1}.

After keeping the mixture for 2 h at 600 °C, the sample was allowed to cool to room temperature and the resulting solids were collected on a filter paper and washed with H_2O (3 x 100 mL). The resulting reddish material was dried at 50 °C.

1.6 Characterization: The X-ray powder diffraction patterns were recorded on Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKα radiation (λ = 0.15418 nm) applying 2θ step size of 0.05° and counting time of 3 s per step. Steady-state UV-Vis absorption spectra were acquired using Shimadzu UV 2600 in diffuse reflectance mode. Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra were recorded on a Varian1000 FT-IR spectrometer equipped with an attenuated total reflection unit with diamond, with a resolution of 4 cm^{-1}. Elemental combustion analysis was performed using a Vario Micro device. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was conducted using a Horiba Ultra 2 instrument equipped with photomultiplier tube detector. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ThermoScientific Escalab 250 Xi. Analyses were conducted using a microfocused, monochromatic Al K α X-ray source (1486.68 eV). The spot size for the analysis was 400 µm. Samples were prepared by dropcasting dispersion of carbon nitride in a solvent on a silicon wafer to avoid the interference of normal carbon tape. LiCl (for Li free samples) or KCl (for Li containing samples) was added as external reference to calibrate the binding energies towards Li or K. ThermoScientific Avantage software was used to analyze the resulting spectra. The band gap was calculated by linear fit of the valence region (0-5 eV) of each material.

For high-resolution transmission electron microscopy (TEM) observations, a suspension of the sample in ethanol was sonicated for 10 minutes and then drop-casted onto a Cu grid with a lacey carbon support and dried for 5 minutes. The TEM study was performed using a double Cs corrected JEOL JEM-ARM200F (S)TEM operated at 80 kV and equipped with a cold-field emission gun.

Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three-electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared on

F-doped tin oxide (FTO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of FTO glass was protected using Scotch tape. The 3 mg sample was dispersed in 1 mL of water by sonication to get a slurry mixture. The slurry was spread onto pretreated FTO glass. After air-drying, the Scotch tape was removed and the working electrode was further dried at 393 K for 2 h to improve adhesion.

1.7 Photocatalytic tests for H_2 production: Photocatalytic H_2 evolution activities were evaluated in a closed system equipped with a pressure detector to examine the pressure of the evolved gases during photocatalytic reactions. White LED light (50 W, $\lambda > 420$ nm), purple LED (50 W, λ = 410 and 420 nm) and Blue LED (50 W, λ = 465 nm) were used for photocatalytic H_2 evolution evaluation, respectively. The used volume of the reactor was 38 mL and the temperature was controlled to be 298 K by cycle water. The evolved amount of H_2 was finally calculated using the Clausius–Clapeyron relation (PV = nRT). Typically, 50 mg of solid catalyst was dispersed into 38 mL of DI water and TEOA (10 Vol. %) mixture, while they were degassed in advance by sonication in vacuum. 3 wt. % of Pt co-catalyst were deposited by a typical *in-situ* photodeposition strategy from H_2PtCl_6 precursor. The H_2 evolution rate was calculated excluding the first reaction hour.

The reuse of the catalyst was performed by separating the catalyst by centrifugation (9000 rpm, 5 min) of the reaction mixture in 50 mL centrifuge tubes. The catalyst was extensively washed with deionized water. After that, the separated catalyst was dried at 60°C under vacuum overnight.

1.8 The AQY measurement and wavelength experiment: H_2 evolution apparent quantum yield (AQY) was measured using a monochromatic visible light (420±1.0 nm). The AQY was calculated as follow:

$$AQY\ (\%) = \frac{2\ x\ r_{H2}\ x\ N_A\ \ x\ h\ x\ c}{S\ x\ I\ x\ \lambda}\ x\ 100$$

where, r_{H2} is the production rate of H_2 molecules (mol s^{-1}), N_A is Avogadro constant (6.022×10^{23} mol^{-1}), h is the Planck constant (6.626×10^{-34} J s^{-1}), c is the speed of light (3×10^8 m s^{-1}), S is the irradiation area (cm^2), I is the intensity of irradiation light (W cm^{-2}) and λ is the wavelength of the monochromatic light (m).

1. ADDITIONAL INFORMATION

Table S1. Elemental composition of long-layered Na-PHI according elemental analysis and ICP-OES data (data in wt. %)

Sample	N (%)	C (%)	H (%)	H_2O (%)[a]	Na (%)	K (%)	Li(%)	C/N (mol/mol)
Na-PHI	40.1(±2.0)	26.0(±2.0)	2.11(±0.7)	15.3(±1.5)	10.4(±2.13)	-	-	0.75
K-PHI	41.8(±2.0)	27.8(±2.0)	1.74(±0.7)	12.3(±1.5)	-	15.6(±0.36)	-	0.76
NCN-K-PHI	41.8(±2.0)	28.0(±2.0)	1.68(±0.7)	12.1(±1.5)	-	11.1(±1.45)	-	0.78
LiK-PHI	40.7(±2.0)	26.5(±2.0)	1.96(±0.7)	14.47(±1.5)	-	9.2(±1.1)	0.9(±0.1)	0.76
CN-OA-m	45.4(±2.0)	29.7(±2.0)	1.88(±0.7)	6.2(±1.5)	-	7.2(±1.1)	1.1(±0.1)	0.76

[a] Calculated from the TGA weight loss data.

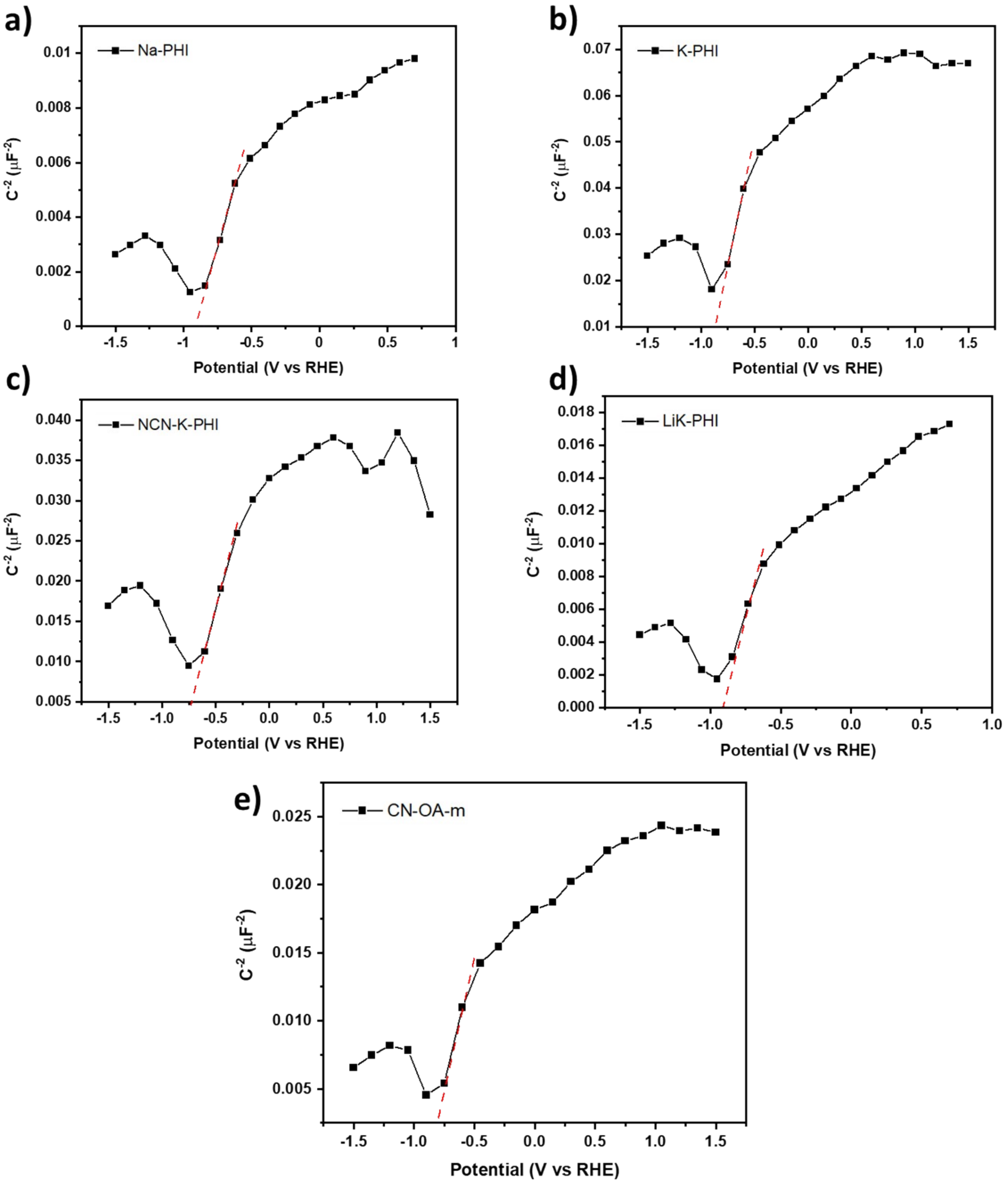

Figure S1. Mott-Schottky plots of **(a)** Na-PHI, **(b)** K-PHI, **(c)** NCN-K-PHI, **(d)** LiK-PHI and **(e)** CN-OA-m.

Table S2. Estimated band positions of Na-PHI, K-PHI, NCN-K-PHI, LiK-PHI and CN-OA-m

Sample	CB (V vs NHE)	VB (V vs NHE)	EBG (eV)
Na-PHI	–0.24	2.54	2.78
K-PHI	–0.46	2.32	2.78
NCN-K-PHI	–0.15	2.62	2.77
LiK-PHI	–0.32	2.36	2.68
CN-OA-m	–0.03	2.29	2.32

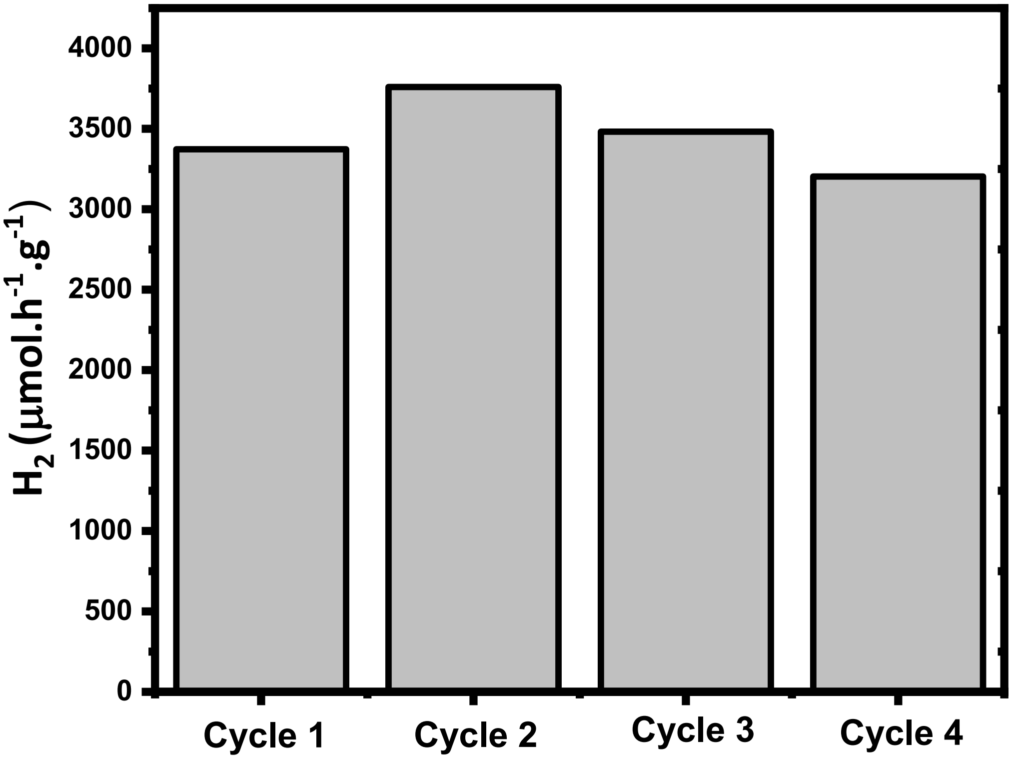

Figure S2. Recyclability tests for Na-PHI in the presence of 0.25 mol L^{-1} LiCl.

2. References

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