# Journal of Materials Chemistry A

Materials for energy and sustainability

### Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Q. Liu, Z. Chen, W. Tao, H. Zhu, L. Zhong, F. Wang, Z. Ren, Y. Lei, C. Liu and X. Peng, *J. Mater. Chem. A*, 2020, DOI: 10.1039/D0TA03870A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

## Edge Activation of Inert Polymeric Carbon Nitride Matrix with Boosted Absorption Kinetic and Near-infrared Response for Efficient Photocatalytic CO<sub>2</sub> Reduction

Qiong Liu<sup>a,b\*</sup>, Zhongxin Chen<sup>b</sup>, Weijian Tao<sup>c</sup>, Haiming Zhu<sup>c</sup>, Linxin Zhong<sup>a</sup>, Fuxian Wang<sup>d</sup>, Ren Zou<sup>a</sup>, Yongqian Lei<sup>d</sup>, Cuibo Liu<sup>b</sup>, Xinwen Peng<sup>a\*</sup>

<sup>a</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of

Technology, Guangzhou 510641, China

<sup>b</sup>Department of Chemistry and Centre for Advanced 2D Materials (CA2DM)

National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

°Centre for Chemistry of High-Performance & Novel Materials, Department of

Chemistry, Zhejiang University

<sup>d</sup>Guangdong Provincial Key Laboratory of Emergency Test for Dangerous Chemicals,

Guangdong Institute of Analysis, Guangzhou 510070, China

#### **Corresponding Author**

\*E-mail: chmv231@nus.edu.sg (Q. Liu); fexwpeng@scut.edu.cn (X. Peng).

Journal of Materials Chemistry A Accepted Manuscript

Abstract: Reduction of CO<sub>2</sub> into C<sub>1</sub> feedstocks (e.g. CO) by utilizing solar energy has attracted increasing attention for the efficient production of renewable energy. While, a significant challenge in CO<sub>2</sub> reduction is achieving with high conversion efficiency due to the high C=O dissociation energy of CO<sub>2</sub> and difficultly inaccessible to the surface of photocatalyst. In the present contribution, we fabricate a polymeric carbon nitride (PCN) catalyst with hydroxyethyl group grafted in the edge via a facile bottom-up strategy, facilitating an efficient surface absorption of CO<sub>2</sub>, lowering the CO<sub>2</sub> transformation energy barrier, accompanying with an exceptional extended optical absorption ability to near-infrared region as well as the increased of state density along the Fermi level. Thus, concentrated CO<sub>2</sub> molecules are able to contact the surface of PCN and easily activated, enables an excellent CO production rate up to 209.24 µmolh<sup>-</sup> <sup>1</sup>g<sup>-1</sup> in the modified PCN (i.e. 39.5 folds' increase than pristine PCN) and a selectivity of 98.5% under the white LED light illumination, exceeding most of the PCN-based energy conversion system reported to date. Notably, this PCN matrix also exhibits photocatalytic CO production activity at the near-infrared region from 780 to 850 nm. These results pave the way to develop structured photocatalysts with easy accessibility of CO<sub>2</sub> and broadband spectral response for efficient photocatalytic CO<sub>2</sub> reduction.

Keywords: polymeric carbon nitride, photocatalytic CO<sub>2</sub> reduction, hydroxyethyl group, edge CO<sub>2</sub> activation, near-infrared response

Journal of Materials Chemistry A Accepted Manuscript

Conversion of CO<sub>2</sub> into valuable chemical fuels by solar-driven photocatalytic strategy is one of the most attractive routes for addressing the problem of global warming and the production of renewable energy <sup>1-4</sup>. Although many photocatalysts have been applied for CO<sub>2</sub> conversion in the previous decades, including metal oxides (TiO<sub>2</sub>, WO<sub>3</sub>, ZnO) <sup>5-9</sup>, metal chalcogenides (CdS) <sup>10-12</sup>, layered double hydroxides <sup>13</sup>, Metal-Organic Framework<sup>14, 15</sup> and layered Bi-based semiconductors <sup>16, 17</sup>. The photocatalytic CO<sub>2</sub> reduction efficiency remains undesired owing to the high activation energy barriers of CO<sub>2</sub> (i.e. high C=O dissociation energy of 750 kJmol<sup>-1</sup> in CO<sub>2</sub> molecule) and relative low selectivity due to multiple electron transfer steps to produce a variety of products as well as the sluggish kinetics for the CO<sub>2</sub> absorption and mass transfer. This requires favorable CO<sub>2</sub> absorption, easy activation, and sufficient excited electron and proton transfers to facilitate subsequent  $CO_2$  reduction processes <sup>18, 19</sup>. With intense studies on photocatalysts, porous layered materials with a high surface area via some modifications may be the candidates for  $CO_2$  reduction <sup>20</sup>. In this case, visible-light-driven polymeric carbon nitride (PCN) has drawn massive attention <sup>21-24</sup> due to its layered structure, chemical stability, and low cost, while the CO<sub>2</sub> reduction rate of pristine PCN is far from satisfactory.

Pioneering studies have revealed improved  $CO_2$  photocatalytic efficiency by combining PCN with other semiconductors <sup>25-27</sup> to facilitate the separation of photoinduced charge carriers. The incorporation of modulated complex cocatalysts such as iron quaterpyridine, cobalt phthalocyanine or binuclear ruthenium (II) complex in the

Journal of Materials Chemistry A Accepted Manuscript

PCN matrix can achieve similar elevated activity <sup>28-31</sup>. Grafted a hydrophobic polymer in the PCN surface to overcome the mass transfer limitation of CO<sub>2</sub>, then proceeding the enhanced CO<sub>2</sub> reduction activity and selectivity <sup>32</sup>. However, attempts on basal plane activation of the PCN matrix remain scarce, where the lack of sufficient active sites on the surface of the catalyst and altered redox ability hampers long-term applications of the above PCN-coupled systems. The introduction of surface defects becomes increasingly important because it helps to tune the chemical and electronic structures of the PCN matrix, to generate more active sites and lower the activation energy of CO<sub>2</sub><sup>33</sup>. Generating carbon vacancies in the PCN matrix provides long-lived photo-generated charges and enhanced reaction kinetics and this can be achieved via a steam-etching approach <sup>34</sup> however, this requires rigorous conditions and breakage of long-range order. On the other hand, when considering the surface termination of incomplete cyclization of heptazines, residual NH2/NH may also serve as the real active sites, which leads to difficulty to activate CO<sub>2</sub> and poor transport of charge carriers <sup>35-</sup> <sup>38</sup>. The replacement of terminal amino groups by cyano groups in a solvothermal process can lead to enhanced activity towards CO<sub>2</sub> reduction <sup>39</sup>. Nonetheless, such modification only allows a weak optical response absorption region (< 500 nm) and insufficient selectivity, severely inhibiting the broadband, solar spectrum-utilization efficiency for the target product <sup>40, 41</sup>. More importantly, although the improved activity is generally achieved by the reported works, but little has been done to optimize the CO<sub>2</sub> absorption kinetics and reduce the CO<sub>2</sub> transformation energy barriers. Although rarely reported, it is evidenced that introducing coordination molecule linkers in the

View Article Online

edge of the material structural unit (e.g. the homogeneous transition photoredox<sup>37/DOTA03870A</sup> catalysts <sup>42</sup> or metal-organic frameworks <sup>43</sup>) is able to change the rate-determining step, modulate the intrinsic affinity and engineer the electronic structure. Bearing the covalent multi-step polymerization processes from cyanamide derivatives during the synthesis of PCN, allowing nucleophilic addition reaction with some electron-rich motifs. These observations inspire that some functional organic linkers can be introduced in the structural units in PCN via a facile bottom-up strategy to modulate the reaction kinetics for  $CO_2$  conversion, but not yet achieved.

Bearing these considerations in mind, we elaborately designed hydroxyethylfunctionalized one dimension PCN nanostructures by applying an organic amine catalyst (*e.g.*, N-acetylethanolamine, NA) into the hydrothermal pretreatment synthetic procedure and then the calcination process. Combining a set of systematic experimental analyses and density functional theory (DFT) calculations, we identify that the replacement of terminal amino groups by hydroxyethyl groups caused by the addition of NA drastically facilitates the absorption capability of CO<sub>2</sub> molecule and reduce the CO<sub>2</sub> transformation energy barrier. And the existence of hydroxyethyl groups enhances the optical absorption capability of the PCN matrix up to the near-infrared region due to the optimized electronic structure and promotes the photo-generated charge separation. This led to a remarkable CO production rate of 209.42  $\mu$ molh<sup>-1</sup>g<sup>-1</sup> (~ 39.5 fold increase compared to that of pristine PCN) together with a selectivity of 98.5% for the NA-modified PCN catalyst and an apparent quantum efficiency of 5.26% at  $\lambda$ =420

nm for photocatalytic  $CO_2$  reduction, together with a extended response activity among the near-infrared region.

#### 2. Experimental Section

#### 2.1. Sample synthesis

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

The HCNT-NA was prepared in the following process, briefly, 3 g of dicyandiamide (DCDA) was added into a 15 mL mixture solution containing 5 mL deionized water and 10 mL propanol, then followed added 0.15 mL Nacetylethanolamine (NA) and stirred for 30 min. Then, the mixture was transferred into a 25 mL stainless steel autoclave (Teflon-lined) and heated at 180 °C for 10 h 44. When natural cooled down, the obtained precipitate was washed by water and ethanol several times, followed dried at 80 °C for 6 h in a vacuum oven. Finally, the intermediate solids were heated to 550 °C at a ramp rate of 10 °C/min and kept for 4 h at the static air atmosphere by using Nabertherm GmbH muffle furnace to obtain polymeric carbon nitride (PCN) sample, named as HCNT-NA. And the g-C<sub>3</sub>N<sub>4</sub> samples via different addition content of NA, such as 0.05, 0.10, 0.15 and 0.20 mL were also prepared, donated as HCNT-NA<sub>1</sub>, HCNT-NA<sub>2</sub>, HCNT-NA<sub>3</sub>, and HCNT-NA<sub>4</sub>. This process for chemical structure variation of synthesizing the HCNT-NA is illustrated in Scheme S1 and **S2**. For comparison, HCN-NA or HCNT was prepared without added propanol or NA under the above same conditions. And a bulk PCN sample (denoted BCN) was synthesized from DCDA by the directly calcined in a muffle furnace at 550 °C/4 h with an elevated rate of 10 °C min<sup>-1</sup>, according to the previous reports, the chemical structure variation along with the elevated temperature is illustrated in Scheme S3.

Journal of Materials Chemistry A Accepted Manuscript

To illustrate the versatile of this modulated synthesis methods, several<sup>®</sup> other<sup>SynDTA03870A</sup> additives were selected including Ethylene glycol (EG), Ethylenediamine (EDA), Ethanolamine (EOA), Diethanolamine (DOA), Triethanolamine (TOA) to react with the precursor, typically, 0.10 mL additive was added into 25 mL aqueous suspension containing 3 g DCDA to dissolve completely, then hydrothermally treated at 180 °C for 10 h. After dried the obtained intermediate solids, continuously heated them at 550 °C 4 h with a 10 °C/min rising rate. Resultant CN-based samples denoted as HCN-EG, HCN-EDA, HCN-EOA, HCN-DOA, and HCN-TOA, respectively. The molecule of selected additives together with the N-acetylethanolamine (NA) is shown in **Scheme S4**. Similar to the synthesis process of HCNT-NA, we also select three additives including EOA, DOA, TOA (0.15 mL) to prepare HCNT-EOA, HCNT-DOA, and HCNT-TOA, respectively.

#### 2.2. General information for Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer by using Cu Kα1 radiation. X-ray photoelectron spectroscopy (XPS) and valence band-XPS spectra were monitored by a Kratos Axis Ulra DLD spectrometer with charge neutralization and equipped with a monochromatic Mg Kα X-ray source, samples were pressed onto a silicon foil and referenced with the adventitious carbon C 1s peak at 284.90 eV. Fourier transform infrared (FT-IR) spectra were obtained by a Bruker Vector 33. Magic Angle Spinning solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on an Agilent VNMRS 600 MHz magnetic resonance spectrometer. CNHO elemental analyses were performed on an Elementar Vario

MICRO analyzer. The morphologies and texturization of the samples were investigated by applying a Hitachi SU8220 scanning electron microscope (SEM) and a JEM-2100 JEOL transmission electron microscope (TEM, 200 kV). The roughness of the surface over the working electrode was measured by Bruker Multimode 8. Surface areas were conducted according to Brunauer-Emmett-Teller (BET) theory from the N2 absorptiondesorption isotherms by using a Micromeritics ASAP 2020 apparatus at 77 K and CO<sub>2</sub> absorption curve at 298 K. Diffuse reflectance UV-Vis spectra (DRS) were recorded Shimadzu U-3010 spectrophotometer, referenced to BaSO<sub>4</sub>. а Static on photoluminescence (PL) emission spectra (375 nm excitation) were acquired with a Hitachi F-4600 fluorescence spectrometer at room temperature.

For femtosecond transient absorption spectroscopy (TA), the fundamental output from Yb: KGW laser (1030 nm, 220 fs Gaussian fit, 100 kHz, Light conversion Ltd) was separated to multiple light beams. One was introduced to a non-collinear optical parametric amplifier and a second harmonic generation crystal BBO to generate a certain wavelength for pump beam (here we use 400 nm). The other was focused on a BBO crystal to generate 515 nm pulses and then focused on a YAG crystal to generation continuum blue light as a probe beam. The temporal delay between them is controlled via a motorized delay stage. The pump and probe pulses overlapped spatially in the sample and the transmitted probe light was collected by a linear array detector.

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

In situ infrared (IR) spectrum was performed on Thermo Fisher Nicolet iS 50 with an in situ Harrick IR cell. The in situ FTIR experiment was performed on a Bruker Tensor II FTIR spectrometer. Firstly, the samples were sealed in the specimen chamber,

View Article Online

then, the 40 mL/min pure CO<sub>2</sub> was followed into the specimen chamber which was  $^{1010397D0TA03870A}$  carrying 10% TOA/acetonitrile aqueous solution with a certain amount of  $[Co(bpy)_2]$  Cl<sub>2</sub>·6H<sub>2</sub>O (bpy=2'2-bipyridine) to simulate the CO<sub>2</sub> photoreduction reaction condition. After 30 min later, the specimen chamber loaded samples were irradiated from the SiO<sub>2</sub> window with a Xe lamp for 1 h and the infrared absorbance spectra were recorded for every 10 minutes.

#### 2.3. Photoelectrochemical measurements

Electrochemical measurements were carried out on a CHI660E electrochemical workstation equipped with a standard three-electrode system, Pt plate as the counter electrode and saturated Ag/AgCl (3.5M KCl) as the reference electrode. The prepared of working electrode was as follows: firstly, using acetone and ethanol to clean the Fdoped thin oxide (FTO) glass, the obtained samples (10 mg) was added into 1 mL ethanol solution with 20 µL of 5% Nafion, sonicated for 30 min to form the homogeneous slurry. Then transferred onto the FTO glass by dipping to achieve a 1\*1 cm<sup>2</sup> active region, followed by heating at 150 °C for 2 h. Supporting electrolytes was 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 6.8), 0.2 M NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> served as the buffer solution. A 300 W Xe-lamp (Beijing ProfectLight, Microsolar300) with a 420 nm cutoff filter was applied as the incident visible light source. The photocurrent-time response (I-t) was conducted in the dark and under the light irradiation by chopping from the 300 W Xe lamp at a bias potential of -0.2 V vs. Ag/AgCl. Moreover, the I-t curves by using the different monochromatic wavelengths light source of 420 nm, 450 nm, 535 nm, 550 nm, 600 nm, 730 nm, 765 nm and 810 nm were also measured.

Electrochemical impedance spectroscopy (EIS) was conducted with an AC<sup>DOL 10,1039/DOTA03870A</sup> amplitude of 10 mV at -0.2 V vs. Ag/AgCl over the frequency range from 10 kHz to 0.01 Hz in the dark. The Mott-Schottky plots were carried out by using the frequency of the AC potential at 3000, 4000 and 5000 Hz. The carrier concentration was calculated from the  $(1)^2$ :

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_D A^2} \left( \Phi_{SC} - \frac{kT}{e} \right) \quad (1)$$

Where e is the elemental charge:  $1.6 \times 10^{-19}$  C, A is the active area of work electrode,  $\varepsilon_0$ is the permittivity of vacuum:  $8.85 \times 10^{-14}$  F/cm,  $\varepsilon$  is the relative permittivity of the material, the value is 5.5 for  $C_3N_4$ . The value of kT/e is too low; it is generally ignored. 2.4. Evaluation of photocatalytic  $CO_2$  reduction

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

Photocatalytic CO<sub>2</sub> reduction was monitored by using a Beijing ProfectLight PCX-50C photochemical reaction device equipped with a 5 W white LED lamp. Typically, 50 mg catalyst, 1µmol CoCl<sub>2</sub>, 15 mg 2,2-bipyridine was added in 3 mL 10% TOA/acetonitrile solution with 0.5 mL H<sub>2</sub>O and ultrasonically dispersed for 15 min. The reactor was degassed three times to vent air and filled into the high pure  $CO_2$  gas (99.999%). Then the reactor was illuminated under the white LED lamp. The gaseous components (CO, CH<sub>4</sub>) were monitored by an FID detector equipped with a mechanized by gas chromatography and the generation of H<sub>2</sub> was simultaneously detected by the TCD detector. Note that the role of the mechanizer was used to convert CO to CH<sub>4</sub> for FID analysis. The liquid products were also detected by the FID detector after reaction by injected 10  $\mu$ L sample, but no product was observed in this work. The reaction temperature was controlled at 26 °C by an liquid cooling system. The isotopic label

View Article Online

experiments reaction is conducted with the same condition mentioned above for dot and the same condition mentioned above for dot above for dot and the same condition mentioned above for dot and the same condition mentioned above for dot above for dot and the same condition mentioned above for dot above for dot and the same condition mentioned above for dot above for dot

For recycling tests. 50 mg catalyst, 1 $\mu$ mol CoCl<sub>2</sub>, 15 mg 2,2-bipyridine was added in 3 mL 10% TOA/acetonitrile solution with 0.5 mL H<sub>2</sub>O, purged with pure CO<sub>2</sub>, and irradiated with white LED lamp. After 4 h, the catalyst was collected by centrifugation at 10,000 rpm for 5 min, washed with acetonitrile and ethanol, after dried, redispersed in fresh TOA/acetonitrile solution with the sample condition, irradiated 4 h again for subsequent 3 recycling runs.

#### 2.5. Calculation of apparent quantum efficiency (AQE)

The apparent quantum efficiency (AQE) for CO evolution was evaluated by using the ProfectLight PCX50B under the illumination of a 5 W LED lamp. The different monochromatic wavelength light was set at 385 nm, 420nm, 465 nm, 500 nm, 550 nm, 595 nm, 630 nm, 730 nm, 785 nm, 810, and 840 nm. Note that the latter three kinds of monochromatic light source of 785 nm, 810, and 840 nm belong to the near-infrared region. The amount of generated CO was collected after the light irradiation lasted for four hours. AQE under the different wavelengths were calculated by the following equation:

$$AQE = \frac{2 \times the \ evolved \ H_2 \ molecules \ number(N_e)}{the \ incident \ photos \ number(N_p)} \times 100\% \ (2)$$

The number of CO molecules can be calculated from the moles of CO of which the generation rate of CO under 420 nm is 5.646 µmolh<sup>-1</sup> and Avogadro's number (6.022

Journal of Materials Chemistry A Accepted Manuscript

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

× 10<sup>23</sup>). Thus, the received electron number of the products:  $2 \times 5.646 \times 10^{9/\text{D0TA03870A}}$ <sup>6</sup>/3600=3.114×10<sup>-9</sup> mols<sup>-1</sup>.

The energy of single-photon at  $\lambda = 420$  nm is calculated to be  $4.736 \times 10^{-19}$  J, according to hc/ $\lambda$ , h and c is the Planck constant and the speed of light. The light intensity was measured to be  $3.44 \text{ mW/cm}^2$  by calibrating with a light power meter (PL-MW2000). The diameter of the illumination window of the reactor was 2.5 cm, then the irradiation area was calculated to be  $4.91 \text{ cm}^2$ . Thus, the total incident photos number can be calculated to be  $5.924 \times 10^{-8} \text{ mols}^{-1}$ . Thus, the AQE= $3.114 \times 10^{-9} \text{ mols}^{-1}$ / $5.924 \times 10^{-8} \text{ mols}^{-1} \times 100\% = 5.26\%$ .

#### 2.6. Calculation of turnover number (TON)

The calculation of turnover number (TON) over Co(bpy)<sub>2</sub>/HCNT-NA was using the following equation:

# $TON = \frac{moles \ of \ evolved \ products \ gas}{moles \ of \ active \ components \ on \ photocatalysts} (3)$

Moles of evolved products gas: herein, only the CO and H<sub>2</sub> were detected as the products of CO<sub>2</sub> reduction. By using the 50 mg Co(bpy)<sub>2</sub>/HCNT-NA catalyst, the photocatalytic activity could relatively maintain stable during 8 h. After the reaction of 8 h, the amount of CO and H<sub>2</sub> were detected to be 83.70  $\mu$ mol and 0.26  $\mu$ mol, respectively. Moles of active components on photocatalysts: the addition of CoCl<sub>2</sub> is 1 $\mu$ mol for 50 mg HCNT-NA. Thus, the TON= (83.70+0.26)  $\mu$ mol/1 $\mu$ mol=83.96, the TON is obviously larger than, demonstrating the catalytic nature of this CO<sub>2</sub> reduction reaction by using HCNT-NA.

#### 2.7. DFT calculations

/iew Article Online

DFT calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized GGA PBE functional, all-electron plane-wave basis sets with an energy cutoff of 400 eV, and a projector augmented wave (PAW) method was adopted. g-C<sub>3</sub>N<sub>4</sub> is simulated using a surface model of p (2 × 2) unit cell periodicity. A (3 × 3 × 1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. 15 Å vacuum layer was added to avoid the interaction between adjacent layers. The electronic density of states (DOS) of (2 × 2) supercells were calculated using a higher 9 × 9 × 1 k-point mesh. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set 1\*10<sup>-4</sup> eV in total energy and 0.05 eV/ Å in force on each atom. The adsorption energy change ( $\Delta E_{abs}$ ) was determined as follows:  $\Delta E_{abs} = E_{total}$ -  $E_{sur}$ -  $E_{mol}$ 

where  $E_{total}$  is the total energy for the adsorption state,  $E_{sur}$  is the energy of pure surface,  $E_{mol}$  is the energy of the molecule.

The free energy change ( $\Delta G$ ) for adsorptions were determined as follows:

 $\Delta G = E_{\text{total}} - E_{\text{sur}} + \Delta E_{\text{ZPE}} - T\Delta S$ 

where  $E_{total}$  is the total energy for the adsorption state,  $E_{sur}$  is the energy of the pure surface,  $\Delta E_{ZPE}$  is the zero-point energy change and  $\Delta S$  is the entropy change.

#### 3. Results and discussion

#### 3.1. Material synthesis and characterization

The synthesis of PCN-based photocatalyst involves two steps: a hydrothermal pretreatment to form a melamine-cyanaurate complex, followed by thermal condensation to obtain NA-modified holey PCN microtubes (HCNT-NA, Fig. 1a).

Hydroxyethyl groups were grafted at the edge of heptazine motifs through<sup>O1.10.1039/D01A03870A</sup> replacement of NH/NH<sub>2</sub> groups by nucleophilic addition with the precursor during hydrothermal pretreatment in a water/propanol mixture (tentative reaction mechanism is illustrated in **Scheme S1**, supporting information). We also synthesized a series of control samples as illustrated in **Scheme S2 & S3**, such as bulk PCN (BCN), holey PCN microtubes (HCNT) and NA-modified holey PCN nanosheets (HCN-NA).

Detailed characterizations on the structural change of pristine and modified PCN have been provided in **Fig. 1b & c**, **Fig. S1**, and **Table S1**. All PCN samples show similar two diffraction peaks (**Fig. S1**), reflecting the periodic packing of in-plane heptazine motifs and the interlayer stacking of lamellar structure, indexed to (100) and (002) lattice face, respectively <sup>45, 46</sup>. Chemically tailored PCN (HCNT-NA) exhibits a slight left shift for both (002) peak and (100) peak than the BCN counterpart due to distorted heptazine motifs and enlarged layered spacing by the grafted hydroxyethyl group and formation of 1D tube structure <sup>47</sup>. Much higher BET specific surface area of HCNT-NA (73.3 m<sup>2</sup>/g versus 9.5 m<sup>2</sup>/g of BCN) is verified by the N<sub>2</sub> adsorption-desorption isotherm (**Fig. S2**) due to the introduction of well-defined mesopores <sup>48</sup>.

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

The successful grafting of hydroxyethyl on the PCN matrix is confirmed by solidstate <sup>13</sup>C magic angle spinning (MAS) NMR in **Fig. 1b**. HCNT-NA shows two characteristic peaks at 154.9 and 164.8 ppm from the C-(N)<sub>3</sub> (*I*) and NH<sub>2</sub>-C(N)<sub>2</sub> (*2*) in heptazine motifs, respectively, and possess slight left shift than BCN <sup>49, 50</sup>. The peak ratio (I<sub>1</sub>/I<sub>2</sub>) gradually increases with the incorporation of NA due to the replacement of NH<sub>2</sub>-C(N)<sub>2</sub> by the hydroxyethyl group (see detailed model structure in the diagram of

**Fig. S5**). This is reflected in two additional peaks at 136.4 and 189.5 ppm in HCNT-NA from the C-C-OH (*3*) and aromatic ring-C-C (*4*) in the hydroxyethyl group <sup>51, 52</sup>, this could be confirmed in previous work which successfully introduced diethylamino groups in heptazine derivatives <sup>53, 54</sup>.

Further evidence of edge-functionalization is provided by high-resolution XPS N<sub>1s</sub> spectra in **Fig. 1c & S4**, where certain peak shifts of the C-N=C, N-(C)<sub>3</sub> and C-N-H species can be observed in HCNT-NA, HCN-NA relative to those in BCN <sup>55</sup>. It is recognized that the C-N heterocycles have a strong polarity, where hydroxyethyl groups serve as electron donors to enhance the  $\pi$ -conjugated, electron-rich system, resulting in the positive shifts in escape energy of surface electrons (binding energy in XPS) <sup>56, 57</sup>. A similar observation can be found in the XPS C<sub>1s</sub> spectra in **Fig. S3**. The binding energy of N-C=N in HCNT-NA, indexed to the in-plane hybridized carbon of the C-N heterocycles, is slightly higher than that of BCN <sup>45, 58</sup>. Although we also acquired the FTIR spectra in **Fig. S1**, the hydroxyethyl group is hard to distinguish from the overlapping  $-NH_2/OH$  groups in 3200-3500 cm<sup>-1</sup> and the C-N heterocycles in 1200-1700 cm<sup>-1 21, 46</sup>. A higher C/N ratio as well as a higher O percentage in HCNT-NA from elementary analysis in **Table S1** also confirms the installation of hydroxyethyl groups on the PCN matrix.

#### 3.2. Morphological characterization

Scanning and transmission electron microscopy (SEM & TEM) were used to observe the morphology of catalysts. As shown in **Fig. 1d**, the intermediate compound of HCNT-NA after hydrothermal treatment of dicyandiamide (DCDA) with NA has a

well-ordered, pillar-like morphology with diameters of  $2 \sim 3 \mu m$ , which is distinct from well-ordered, pillar-like morphology with diameters of  $2 \sim 3 \mu m$ , which is distinct from well-ordered pillar and the second s the large, irregular particles from DCDA precursor in Fig. S6. This is attributed to the transformation into a modified melamine-cyanaurate complex (see Fig. S7 & S8 for XRD and FTIR) via liquid-liquid supramolecular self-assembling process during hydrothermal treatment 59,60. The modified PCN samples (HCNT-NA) can maintain its 1D hexagonal pillar structure (Fig. 1e) after calcination due to the thermal stability of intermediate compounds, despite volume shrinkage by the release of NH<sub>3</sub> and H<sub>2</sub>O. SEM images at higher magnifications further reveal the packing of leaf-like nanostructures to form the hexagonal entity (Fig. 1f), where vertically aligned nanoarrays are observed on the surface (Fig. 1g), which will form the spatial potential difference to boost the directional charge transfer and the absorption of CO<sub>2</sub><sup>61</sup>. Such a unique mesoporous structure with hollow microchannels within the individual "leaf" provides sufficient active sites for the activation of CO<sub>2</sub> and facilitates the mass transfer of reactants, <sup>36, 61</sup>. Further insight on the microstructure was displayed in the TEM images in Fig. 1h-1l. The 1D porous network is comprised of regularly packed 2D nanosheets with a uniform dimension and a well-ordered high crystalline domain. Bright diffraction patterns in corresponding selected area electron diffraction (SAED) indicate relatively high crystallinity of HCNT-NA, where NA is critical for the formation of high-quality crystals (see the difference of SAED patterns in HCN-NA and HCNT in Fig. S10). Such ordered packing configuration is beneficial for the rapid transfer of photo-induced carriers and the extended optical absorption 62-65. STEM-EDS mapping also confirms the uniform distribution of C, N, and O in HCNT-NA

throughout the selected area.

#### 3.3. Optical absorption and band-gap structure

The optical absorption property of catalysts has been investigated by the UV-vis diffuse reflectance spectra (DRS) in Fig. 2a. Owing to quantum confinement and higher specific surface area, the modified PCN matrix exhibit a slight blue shift in the absorption edge than BCN counterpart <sup>34, 66</sup>. HCNT-NA shows the highest absorption at  $\lambda > 460$  nm with an extended absorption up to near-infrared region due to the formation of an intermediate band in the n- $\pi^*$  state transition, increased density of band tail states, as well as well redistributed localized states (vide infra), resulting in excitations by photons with induced energy lower than the intrinsic band-band transition. Similar results were found in the photoluminescence (PL) spectra and band structure (Fig. S11  $\sim$  S13, see the related discussions in section 4 of supporting information). The profound extension in optical region response leads to a higher concentration of excited electron to facilitate the CO<sub>2</sub> conversion rate. XPS valence band (VB) spectra and Mott-Schottky (M-S) measurements were conducted to elucidate the change in band-edge position. As shown in Fig. 2b, the VB position to the Fermi level shifts positively in HCN-NA (2.16 eV) and HCNT-NA (2.19 eV) than BCN (1.89 eV) <sup>67</sup>. For n-type semiconductors, the conduction band (CB) position can be estimated from the flat potential (0.1-0.2 V lower than CB) by extrapolating the x-axis intercept in the M-S plot 68, 69. As depicted in Fig. 2c, the flat potential of HCNT-NA is obviously less negative than that of BCN (-1.20 versus -1.53 V vs. Ag/AgCl). Importantly, HCNT-NA also has a lower slope in M-S plots, demonstrating its higher

donor carrier density than BCN (1.88\*10<sup>21</sup> versus 7.38\*10<sup>20</sup>, calculation process shown<sup>21</sup> below **Fig. S15**). Such a 2.55-fold increase in carrier donor density is beneficial for subsequent photocatalytic reduction process <sup>64</sup>. Based on the above results, the band diagrams of HCNT-NA and BCN were proposed in **Fig. 2d**.

To reveal the critical role of hydroxyethyl group on the modification of electronic structure, density functional theory (DFT) calculations on the total and partial density of states (PDOS) of catalysts were performed in Fig. 2e & 2f (see DFT models in Fig. S16). After installation of the hydroxyethyl group on the tri-s-triazine units, the CB and VB positions of PCN-NA shifted downwards together with a smaller bandgap than pristine PCN, in good accordance with the XPS-VB and M-S observations. The appearance of an intermediate band from the C<sub>2p</sub> and N<sub>2p</sub> orbitals in PCN-NA agrees with the extended absorption tail along the optical region <sup>35, 70</sup>, and leading to a significant shorten electron transportation distance for the photo-generated carriers <sup>40</sup>. Note that the formation of intermediate band states may be also arouse from the wellordered high-crystalline structure in HCNT-NA, but it is difficult to be quantitated <sup>64</sup>. The density of state along the Fermi level is also significantly increased which is ascribed to the redistributed localized electronic states below the CBM, suggesting a higher concentration of charge carriers <sup>71</sup>. This a high density of localized states associated with the band tails states further contribute to the continuum extension optical region. Additionally, the transient-state photocurrent in Fig. S17 manifests a high carrier separation efficiency in HCNT-NA due to the modulation in the electronic structure after the installation of hydroxyethyl groups. Such extended absorption ability,

intensive concentration of charge carrier and promoted charge separation  $\stackrel{\text{View Article Online}}{=}$  efficient activation of CO<sub>2</sub> on HCNT-NA under visible light.

#### 3.4. Photocatalytic activity evaluation and mechanism analysis

We examined the photocatalytic efficiency of PCN-based catalysts for CO<sub>2</sub> reduction under a 5 W white LED lamp with Co complex as cocatalyst and triethanolamine (TOA) as the electron donor (reaction setup seen in Fig. S18). As shown in Fig. 3a, BCN has an undesired CO production rate of 5.29 µmolh<sup>-1</sup>g<sup>-1</sup> owing to the inert surface for CO<sub>2</sub> activation. Self-assembling into PCN microtubes led to a moderate improvement to 43.91 µmolh<sup>-1</sup>g<sup>-1</sup> for HCNT. Surprisingly, the incorporation of NA into the PCN matrix can dramatically boost the photocatalytic CO<sub>2</sub> reduction, where 24.4 and 39.5 folds increases in the CO yields (129.08 & 209.24  $\mu$ molh<sup>-1</sup>g<sup>-1</sup>) together with a selectivity of ~ 97.5% are observed for HCN-NA and HCNT-NA relative to BCN. Considering their similar specific surface areas, edge activation of the inert PCN matrix by NA functionalization should be the main cause for such improvement. This is confirmed by strong correlations between NA content and CO<sub>2</sub> activity in Fig. S19. Control experiments in Fig. S20-S23 reveal that the catalyst, cocatalyst, TOA, light source, and CO<sub>2</sub> gas are all essential for such a reduction reaction. The PCN catalyst serve as the photocatalysts and the Co complex as the cocatalyst. Under the illumination of white light, the excited electron from PCN would transfer to the Co complex. The <sup>13</sup>C isotopic experiments in the inset of Fig. 3b confirm the generated <sup>13</sup>CO gas at m/z=29 in a mass spectrum is originated from the used  ${}^{13}CO_2$ . HCNT-NA also shows excellent cycling stability for photocatalytic CO<sub>2</sub> reduction,

Journal of Materials Chemistry A Accepted Manuscript

where no obvious change in the structure and morphology could be found in the XRD<sup>/DOTA03870A</sup> and FTIR even after 4 cycles (**Fig. S24 & S25**).

Along with its excellent activity, HCNT-NA exhibits a remarkable apparent quantum efficiency (AOE) at  $\lambda$ =420 nm (5.26%) in Fig. 3b (see the *experimental* section 1.5 in supporting material), outperforming most of the state-of-art heterogeneous photocatalysts for CO<sub>2</sub> reduction in Table S2. The turnover numbers (TONs) when HCNT-NA was used as the catalyst is calculated to be 83.96 for the evolved products over 8 h (see the *experimental section 1.6* in supporting material), demonstrating the catalytic nature of this CO<sub>2</sub> reduction reaction. CO production can be extended to longer wavelengths ( $500 \sim 850$  nm), whereas the detectable amount of CO gas is generated even in the near-infrared region such as  $\lambda$ =785, 810 and 840 nm using HCNT-NA. This is further verified by the observation of recycled transient photocurrent response with the chopped light under near-infrared region (Fig. S26) and time-dependent of CO product evolution at  $\lambda$ =785,  $\lambda$ =810, and  $\lambda$ =840 nm (Fig. S27) over HCNT-NA. To the best of our knowledge, this is the first case using the PCNbased photocatalysts system for the CO<sub>2</sub> conversion in the near-infrared region. Considering the redox potential of CO<sub>2</sub>/CO is as high as -0.53 V. vs NHE, the photocatalytic activity in the near-infrared region may contribute to the formation of inter-band excitation and the nonlinear two-photon responsive <sup>43, 72</sup>.

In order to illustrate the versatility of our functionalized-activation strategy, five different additives such as ethylene glycol (EG), ethylenediamine (EDA), ethanolamine (EOA), diethanolamine (DOA) and triethanolamine (TOA) were chosen (the molecule

View Article Online

structure shown in **Scheme S3**) and reacted with the DCDA precursor. As expected, aff<sup>T/DOTA03870A</sup> of them produce a much higher CO production than BCN in **Fig. 3c**, revealing the universal applicability of in-situ C-N coupling for photocatalytic CO<sub>2</sub> reduction. Additionally, when considering the different molecular structures of EDA and EOA, HCN-EDA (modified by ethyl) and HCN-EOA (modified by hydroxyethyl) delivered a similar CO evolution rate. It suggests that the improved photocatalytic activity is mainly determined by the grafting of the ethyl group, rather than the modification by hydroxy group <sup>73</sup>. While the grafted hydroxyethyl group of HCN-EOA has a slightly enhanced activity than HCN-EDA which implies that the presence of hydroxy also favors CO<sub>2</sub> reduction.

We performed the CO<sub>2</sub> absorption capacity test, in-situ FTIR measurements, and density functional theory (DFT) calculations to understand the catalytic origin of our catalyst. As shown in **Fig. 3d**, HCNT-NA shows the strongest absorption capability toward CO<sub>2</sub>, which is five times larger than that of BCN (5.49 versus 0.95 cm<sup>3</sup>/g), demonstrating a much enhanced CO<sub>2</sub> absorption. Such preferred absorption of CO<sub>2</sub> on the surface of HCNT-NA is validated by the in-situ FTIR spectra in **Fig. 3e**. A series of infrared peaks ascribed to carbonate species were observed under illumination. Specifically, the peaks at 1540, 1513 and 1462 cm<sup>-1</sup> (m-CO<sub>3</sub><sup>2-</sup>), 1337, 1635 cm<sup>-1</sup> (b-CO<sub>3</sub><sup>2-</sup>), 1209, 1406 and 1574 cm<sup>-1</sup> (hydroxyl groups of carboxylic acid) are key evidence of the presence of surface-absorbed COOH\* species <sup>74</sup>. Such COOH\* species is the critical intermediate during the surface activation of CO<sub>2</sub>, whose intensity keeps constant after 10 mins due to a fast equilibrium between COOH\* and the final product

(CO). Meanwhile, the characteristic peak of CO at 2054 cm<sup>-1</sup> gradually increases with time, in good agreement with higher CO production under prolonged illumination (**Fig. S28**).

To further reveal the influence of the hydroxyethyl group on the absorption and activation of  $CO_2$ , the Gibbs free energy involving the reduction pathways of  $CO_2$  to CO via COOH\* were calculated by DFT calculations in Fig. 3f. The results confirm much lower absorption energy of  $CO_2$  on HCNT-NA than BCN (-0.292 versus -0.187 eV), demonstrating the facile activation of CO<sub>2</sub> on HCNT-NA to form COO\*. Detailed models on each CO<sub>2</sub> reduction intermediate are presented in Fig. S29. The activation energy barrier for COOH\* formation over HCNT-NA is slightly smaller than BCN (0.853 versus 0.869 eV, Table S3), indicating that HCNT-NA is also kinetically more favorable for the formation of COOH\* than the BCN counterpart <sup>75, 76</sup>. As shown in the charge difference contours in Fig. 3g & 3h, the presence of hydroxyethyl group can significantly enhance the charge density around adjacent nitrogen atoms in HCNT-NA, of which the charge distribution is clearly more delocalized to interact with the intermediates in CO<sub>2</sub> reduction. This enables a closer C=O bond to catalyst surface for subsequent electron transfer and generation of \*COOH intermediate, thus promoting the overall reduction process. We also calculated the carried charge ( $\Delta q$ ) to estimate the electron transport direction, where the negative value reflects the number of electrons transferred to the CO<sub>2</sub> molecule <sup>16</sup>. Apparently, HCNT-NA has a larger absolute value (-0.391 e) than BCN (-0.129 e), inferring stronger electron transfer to active CO<sub>2</sub> molecules. Collectively, the existence of hydroxyethyl in the structural edge

of HCNT-NA is in favor of CO<sub>2</sub> adsorption, provides more excited electron to active  $CO_2$  molecules and lowers the CO<sub>2</sub> transformation energy barrier.

Finally, the carrier dynamics during the photocatalytic process were investigated by femtosecond transient absorption (TA) spectroscopy in Fig. 4 to understand the importance of the hydroxyethyl group on the movement of charge carriers. After the excitation at 400 nm, both BCN and HCNT-NA display a ground state bleach signal and an excited state absorption signal. The ground state bleach signal in HCNT-NA is broader than BCN and further extends to 440 nm in **Fig. 4c**, inconsistent with the studies on the band structure. The color contours of TA spectra display much stronger positive absorption in HCNT-NA from its higher excited charge carrier density <sup>77, 78</sup>. Since the ground state bleaching originated from the state filling and reflects the excited state carrier population, the carrier dynamics from this signal has been subtracted and plotted in Fig. 4d. It is clearly seen that the lifetime of excited state carriers is substantially prolonged by an order of magnitude (from 2.62 ps to 21.83 ps) with the modification of the hydroxyethyl group. Such a prolonged period for carrier transportation to the interface allows a better charge separation efficiency to provide sufficient surface electrons to participate in the CO<sub>2</sub> reduction.

In this regard, the experimental results can be well illustrated by the introduced of hydroxyethyl groups at the edge and the simultaneous formed the porous 1D microtube with hollow micro-channels as well as the accompanying high crystalline well-ordered domain by using a feasible bottom-up strategy of that endured the NA motifs nucleophilic addition and hydrothermal pretreatment process. On the basis of

aforementioned experimental analyses and theoretical calculations, this Unique structure in HCNT-NA enables the substantially improved photocatalytic CO<sub>2</sub> conversion, as proposed following i) the existence of hydroxyethyl in the structural edge is in favor of CO<sub>2</sub> absorption and lowers the CO<sub>2</sub> transformation energy barrier; ii) The generated inter-band states, increased density of band tail and localized states originated from the hydroxyethyl group and well-ordered mesocrystal structure leads to continuously extended optical region from 450-850 nm; iii ) The lifetime of excited state carriers is substantially prolonged than that of pristine PCN; iv) the functionalized structure accompanied with hierarchy porous 1D microtube can largely limit the radiative recombination of photoinduced electron-hole pairs and facilitate the rapid charge transfer. While, in general, when considering the involved three essential steps in the semiconductor-based photocatalytic CO<sub>2</sub> reduction reaction, namely: i) light absorption, ii) charge carriers separation and transfer, and iii) surface absorption and redox reaction, the enhanced optical absorption region, excellent carriers separation and boosted CO<sub>2</sub> absorption capacity in HCNT-NA, as a result, lead to a significantly photocatalytic performance for CO<sub>2</sub> reduction.

#### 4. Conclusions

Published on 20 May 2020. Downloaded by Uppsala University on 5/21/2020 8:42:32 AM.

In conclusion, We have developed a covalent functionalization strategy to promote the photocatalytic  $CO_2$  reduction on carbon nitride by activating the inert amino edge with the hydroxyethyl group. As synthesized hydroxyethyl functionalized of one dimensional, mesoporous matrix (HCNT-NA) exhibited 39.5 folds' increase in the CO production rate (209.24  $\mu$ molh<sup>-1</sup>g<sup>-1</sup>) than pristine BCN, together with a CO selectivity

Journal of Materials Chemistry A Accepted Manuscript

/iew Article Online

of 98.5% under the white LED light illumination. The hydroxyethyl group at the edge of the CN matrix leads to the formation of an intermediate band in the energy gap and a higher state density along the Fermi level as well as the well-ordered mesocrystal structure, thus enabling stronger light-harvesting ability up to the near-infrared region. The presence of the hydroxyethyl group also promotes the activation of  $CO_2$  by decreasing its absorption energy barrier and activation energy. Meanwhile, the prolonged period for carrier transportation to the interface allows a better charge separation efficiency in HCNT-NA to provide sufficient surface electrons to participate in the CO<sub>2</sub> reduction. Our findings indicate the great potential for using the hydroxyethyl functionalized PCN in visible-light-driven photocatalytic CO<sub>2</sub> conversion and also provide a feasible bottom-up strategy for simultaneously realizing the activation of CO<sub>2</sub> and wide-spectrum optical absorption of strong photoredox ability in the photocatalysts.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgment

X.W. Peng thanks for the National Natural Science Foundation of China (31971614, 31430092, 21736003), Guangdong Natural Science Funds for Distinguished Young Scholar (2016A030306027), Guangdong Natural Science Funds (2017A030313130), Guangzhou science and technology funds (201904010078). F. Wang thanks the National Natural Science Foundation of China (21707128, 61904167). The authors

would like to thank Shiyanjia Lab (www.shiyanjia.com) for the support of DFT DFT calculation.

#### References

- 1. J. Gu, C.-S. Hsu, L. Bai, H. M. Chen and X. Hu, *Science*, 2019, **364**, 1091-1094.
- J. K. Stolarczyk, S. Bhattacharyya, L. Polavarapu and J. Feldmann, ACS Catal., 2018, 8, 3602-3635.
- 3. K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *ChemSusChem*, 2008, 1, 893-899.
- 4. S. Tian, F. Yan, Z. Zhang and J. Jiang, *Sci. Adv.*, 2019, **5**, eaav5077.
- 5. H. Huang, J. Lin, G. Zhu, Y. Weng, X. Wang, X. Fu and J. Long, *Angew. Chem. Int. Ed.*, 2016, **55**, 8314-8318.
- S. Sun, M. Watanabe, J. Wu, Q. An and T. Ishihara, J. Am. Chem. Soc., 2018, 140, 6474-6482.
- 7. Z. Geng, X. Kong, W. Chen, H. Su, Y. Liu, F. Cai, G. Wang and J. Zeng, *Angew. Chem. Int. Ed.*, 2018, **57**, 6054-6059.
- 8. L. Wang, S. Duan, P. Jin, H. She, J. Huang, Z. Lei, T. Zhang and Q. Wang, *Appl. Catal.*, *B.*, 2018, **239**, 599-608.
- L. Wang, P. Jin, S. Duan, H. She, J. Huang and Q. Wang, Sci. Bull., 2019, 64, 926-933.
- 10. C. Bie, B. Zhu, F. Xu, L. Zhang and J. Yu, Adv. Mater., 2019, 31, 1902868.
- 11. H. She, H. Zhou, L. Li, Z. Zhao, M. Jiang, J. Huang, L. Wang and Q. Wang, *ACS Sustainable Chem. Eng.*, 2019, 7, 650-659.
- 12. S. Wang, B. Y. Guan and X. W. D. Lou, *J. Am. Chem. Soc.*, 2018, **140**, 5037-5040.
- 13. L. Tan, S. M. Xu, Z. Wang, Y. Xu, X. Wang, X. Hao, S. Bai, C. Ning, Y. Wang and W. Zhang, *Angew. Chem. Int. Ed.*, 2019, **131**, 11986-11993.
- 14. H. Zhang, J. Wei, J. Dong, G. Liu, L. Shi, P. An, G. Zhao, J. Kong, X. Wang and X. Meng, *Angew. Chem. Int. Ed.*, 2016, **55**, 14310-14314.
- G. Xu, H. Zhang, J. Wei, H.-X. Zhang, X. Wu, Y. Li, C. Li, J. Zhang and J. Ye, ACS nano, 2018, 12, 5333-5340.
- L. Hao, L. Kang, H. Huang, L. Ye, K. Han, S. Yang, H. Yu, M. Batmunkh, Y. Zhang and T. Ma, *Adv. Mater.*, 2019, **31**, 1900546.
- 17. Y. He, H. Rao, K. Song, J. Li, Y. Yu, Y. Lou, C. Li, Y. Han, Z. Shi and S. Feng, *Adv. Func. Mater.*, 2019, **29**, 1905153.
- J. Li, G. Chen, Y. Zhu, Z. Liang, A. Pei, C.-L. Wu, H. Wang, H. R. Lee, K. Liu and S. Chu, *Nat. Catal.*, 2018, 1, 592.
- C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. G. de Arquer, A. Kiani, J. P. Edwards, P. De Luna and O. S. Bushuyev, *Science*, 2018, 360, 783-787.

- 20. N. N. Vu, S. Kaliaguine and T. O. Do, Adv. Func. Mater., 2019, 29, 1901.825. View Article Online Online Contract State State Contract State State Contract State Contra
- 21. B. V. Lotsch and W. Schnick, *Chem. Eur. J.*, 2007, **13**, 4956-4968.
- 22. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.
- F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang and M. J. Bojdys, *Nat. Rev. Mater.*, 2017, 2, 17030.
- L. Shi, K. Chang, H. Zhang, X. Hai, L. Yang, T. Wang and J. Ye, *Small*, 2016, 12, 4431-4439.
- Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao and P. K. Wong, *Adv. Mater.*, 2018, 30, 1706108.
- 26. S. Tonda, S. Kumar, M. Bhardwaj, P. Yadav and S. Ogale, *ACS Appl. Mater. Interfaces*, 2018, **10**, 2667-2678.
- 27. D. Liu, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Angew. Chem. Int. Ed.*, 2020, **59**, 4519-4524.
- 28. R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, J. Am. Chem. Soc., 2016, **138**, 5159-5170.
- R. Kuriki, M. Yamamoto, K. Higuchi, Y. Yamamoto, M. Akatsuka, D. Lu, S. Yagi, T. Yoshida, O. Ishitani and K. Maeda, *Angew. Chem. Int. Ed.*, 2017, 56, 4867-4871.
- C. Cometto, R. Kuriki, L. Chen, K. Maeda, T.-C. Lau, O. Ishitani and M. Robert, *J. Am. Chem. Soc.*, 2018, **140**, 7437-7440.
- 31. S. Roy and E. Reisner, Angew. Chem. Int. Ed., 2019, 131, 12308-12312.
- A. Li, Q. Cao, G. Zhou, B. V. Schmidt, W. Zhu, X. Yuan, H. Huo, J. Gong and M. Antonietti, *Angew. Chem. Int. Ed.*, 2019, 58, 14549-14555.
- 33. S. Bai, N. Zhang, C. Gao and Y. Xiong, *Nano Energy*, 2018, **53**, 296-336.
- P. Yang, H. Zhuzhang, R. Wang, W. Lin and X. Wang, *Angew. Chem. Int. Ed.*, 2019, **131**, 1146-1149.
- V. W.-h. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum and B. V. Lotsch, *Nat. Commun.*, 2016, 7, 12165.
- V. W.-h. Lau, V. W.-z. Yu, F. Ehrat, T. Botari, I. Moudrakovski, T. Simon, V. Duppel, E. Medina, J. K. Stolarczyk, J. Feldmann, V. Blum and B. V. Lotsch, *Adv. Energy. Mater.*, 2017, 7, 1602251.
- Y. Kang, Y. Yang, L.-C. Yin, X. Kang, L. Wang, G. Liu and H.-M. Cheng, *Adv. Mater.*, 2016, 28, 6471-6477.
- 38. Q. Liu, L. Wei, Q. Xi, Y. Lei and F. Wang, Chem. Eng. J., 2020, 383, 123792.
- P. Xia, M. Antonietti, B. Zhu, T. Heil, J. Yu and S. Cao, *Adv. Func. Mater.*, 2019, **29**, 1900093.
- 40. L. Liang, X. Li, Y. Sun, Y. Tan, X. Jiao, H. Ju, Z. Qi, J. Zhu and Y. Xie, *Joule*, 2018, **2**, 1004-1016.
- 41. X. Wu, Y. Li, G. Zhang, H. Chen, J. Li, K. Wang, Y. Pan, Y. Zhao, Y. Sun and Y. Xie, *J. Am. Chem. Soc.*, 2019, **141**, 5267-5274.
- 42. Y. Liu and C. C. L. McCrory, Nat. Commun., 2019, 10, 1683.
- 43. J. Yu, Y. Cui, C.-D. Wu, Y. Yang, B. Chen and G. Qian, *J. Am. Chem. Soc.*, 2015, **137**, 4026-4029.

- 44. Q. Liu, X. Wang, Q. Yang, Z. Zhang and X. Fang, *Appl. Surf. Sci.*, 2018, **1450** (September 2017) 46-56.
- 45. T. Miller, A. B. Jorge, T. Suter, A. Sella, F. Corà and P. McMillan, *Phys. Chem. Chem. Phys.*, 2017, **19**, 15613-15638.
- 46. T. Komatsu, J. Mater. Chem., 2001, 11, 799-801.

- 47. Z. Zeng, Y. Su, X. Quan, W. Choi, G. Zhang, N. Liu, B. Kim, S. Chen, H. Yu and S. Zhang, *Nano Energy*, 2020, **69**, 104409.
- 48. Q. Liang, Z. Li, X. Yu, Z.-H. Huang, F. Kang and Q.-H. Yang, *Adv. Mater.*, 2015, **27**, 4634-4639.
- 49. B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125**, 10288-10300.
- 50. X. Li, I. V. Sergeyev, F. Aussenac, A. F. Masters, T. Maschmeyer and J. M. Hook, *Angew. Chem. Int. Ed.*, 2018, **130**, 6964-6968.
- 51. A. Schwarzer and E. Kroke, *New J. Chem.*, 2011, **35**, 953-958.
- 52. T. Hagiwara, M. Yamaura and K. Iwata, Synth. Met., 1988, 26, 195-201.
- 53. B. Traber, T. Oeser, R. Gleiter, M. Goebel and R. Wortmann, *Eur. J. Org. Chem.*, 2004, **2004**, 4387-4390.
- 54. A. Schwarzer, T. Saplinova and E. Kroke, *Coord. Chem. Rev.*, 2013, **257**, 2032-2062.
- H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung and T. Zhang, *Adv. Mater.*, 2017, 29, 1605148.
- 56. K. Akaike, K. Aoyama, S. Dekubo, A. Onishi and K. Kanai, *Chem. Mater.*, 2018, **30**, 2341-2352.
- 57. C. Ronning, H. Feldermann, R. Merk, H. Hofsäss, P. Reinke and J. U. Thiele, *Phys. Rev. B*, 1998, **58**, 2207-2215.
- 58. A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl and J. M. Carlsson, *J. Mater. Chem.*, 2008, **18**, 4893-4908.
- 59. M. Shalom, S. Inal, C. Fettkenhauer, D. Neher and M. Antonietti, *J. Am. Chem. Soc.*, 2013, **135**, 7118-7121.
- 60. J. Sun, J. Xu, A. Grafmueller, X. Huang, C. Liedel, G. Algara-Siller, M. Willinger, C. Yang, Y. Fu and X. Wang, *Appl. Catal., B*, 2017, **205**, 1-10.
- Z. Lin, Y. Zhao, J. Luo, S. Jiang, C. Sun and S. Song, *Adv. Func. Mater.*, 2020, 30, 1908797.
- 62. L. Lin, Z. Yu and X. Wang, Angew. Chem. Int. Ed., 2018, 58, 6164-6175.
- 63. Q. Liu, X. Wang, Q. Yang, Z. Zhang and X. Fang, *Appl. Catal.*, *B*, 2018, **225**, 22-29.
- H. Wang, X. Sun, D. Li, X. Zhang, S. Chen, W. Shao, Y. Tian and Y. Xie, J. Am. Chem. Soc., 2017, 139, 2468-2473.
- W. Che, W. Cheng, T. Yao, F. Tang, W. Liu, H. Su, Y. Huang, Q. Liu, J. Liu,
  F. Hu, Z. Pan, Z. Sun and S. Wei, *J. Am. Chem. Soc.*, 2017, 139, 3021-3026.
- J. Ran, T. Y. Ma, G. Gao, X.-W. Du and S. Z. Qiao, *Energy Environ. Sci.*, 2015, 8, 3708-3717.
- 67. A. Suzuki, Y. Hirose, S. Nakao and T. Hasegawa, *Chem. Mater.*, 2018, **30**, 8789-8794.

- 68. W.-J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. N. Kondo, M. Hara, M<sup>view Article Online</sup> Kawai, Y. Matsumoto and K. Domen, *J. Phys. Chem. B*, 2003, **107**, 1798-1803.
- 69. A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, 2002, **124**, 13547-13553.
- 70. J. Wirth, R. Neumann, M. Antonietti and P. Saalfrank, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15917-15926.
- 71. W. Wei and T. Jacob, *Phys. Rev. B*, 2013, **87**, 085202.
- 72. Q. Cui, Y. Li, J. Chang, H. Zhao and C. Xu, *Laser Photon Rev.*, 2019, **13**, 1800225.
- 73. S. Yu, J. Li, Y. Zhang, M. Li, F. Dong, T. Zhang and H. Huang, *Nano Energy*, 2018, **50**, 383-392.
- 74. X. Li, Y. Sun, J. Xu, Y. Shao, J. Wu, X. Xu, Y. Pan, H. Ju, J. Zhu and Y. Xie, *Nat. Energy.*, 2019, **4**, 690-699.
- 75. B. Han, X. Ou, Z. Deng, Y. Song, C. Tian, H. Deng, Y.-J. Xu and Z. Lin, *Angew. Chem. Int. Ed.*, 2018, **57**, 16811-16815.
- 76. J. Di, C. Chen, S.-Z. Yang, S. Chen, M. Duan, J. Xiong, C. Zhu, R. Long, W. Hao, Z. Chi, H. Chen, Y.-X. Weng, J. Xia, L. Song, S. Li, H. Li and Z. Liu, *Nat. Commun.*, 2019, **10**, 2840.
- 77. X.-D. Wang, Y.-H. Huang, J.-F. Liao, Y. Jiang, L. Zhou, X.-Y. Zhang, H.-Y. Chen and D.-B. Kuang, *J. Am. Chem. Soc.*, 2019, **141**, 13434-13441.
- L. Liang, X. Li, J. Zhang, P. Ling, Y. Sun, C. Wang, Q. Zhang, Y. Pan, Q. Xu, J. Zhu, Y. Luo and Y. Xie, *Nano Energy*, 2020, 69, 104421.



**Fig. 1.** (a) Schematic illustration for the fabrication of HCNT-NA. (b) Solid-state <sup>13</sup>C MAS NMR spectra, (I) BCN, (II) HCNT-NA<sub>2</sub> and (III) HCNT-NA<sub>4</sub>, the subscript number in HCNT-NA means the addition of different content of NA. Inset images are the enlargement of peak 3 and 4, \*represents the spinning sidebands in the <sup>13</sup>C spectra. (c) XPS high resolution spectra of N 1*s* of BCN and HCNT-NA. SEM images of intermediate of HCNT-NA (d) and HCNT-NA (e). (f) and (g) The close-up of areas marked in (e). (h) TEM image of HCNT-NA. (i) The close-up of areas marked in (h), inset is correspondingly selected area electron diffraction (SAED) pattern. (j) TEM

image of a cross section diagram. (k) STEM C, N and O elements mapping and (1)1 HR 9/DOTA03870A TEM (high resolution) of HCNT-NA.



**Fig. 2.** (a) DRS spectra of BCN, HCNT, HCN-NA, and HCNT-NA. (b) XPS valence band spectra. (c) Mott–Schottky plots over different frequencies of 3000, 4000, 5000 Hz within  $0.5M \text{ Na}_2\text{SO}_4$  and 0.2M phosphate buffer electrolyte of BCN and HCNT-NA. (d) Relative band alignments of HCNT-NA and BCN. Total and partial density of states over (e) CN (BCN) and (f) CN-NA (HCNT-NA), respectively.



Fig. 3. (a) Time dependent of  $CO_2$  reduction products evolved rate of BCN, HCNT, HCN-NA and HCNT-NA. (b) Apparent quantum efficiency of HCNT-NA (irradiated by the LED lamps with different monochromatic wavelengths of 385 nm, 420 nm, 465 nm, 500 nm, 550 nm, 595 nm, 630 nm, 730 nm, 765 nm and 810 nm). Inset is mass spectra of  ${}^{13}$ CO (m/z=29) over HCNT-NA with 4 h illumination by using white LED. (c) Average gas evolved rate of different photocatalyst samples by using the different additives including Ethylene glycol (EG), Ethylenediamine (EDA), Ethanolamine Diethanolamine (DOA), Triethanolamine (TOA) to (EOA), prepare the correspondingly CN-based samples, (1) HCN-EG, (2) HCN-EDA, (3) HCN-EOA, (4) HCN-DOA, (5) HCN-TOA, (6) HCN-NA, (III) HCNT-EOA, (IV) HCNT-DOA, (V) HCNT-TOA and (VI) HCNT-NA. (d) CO<sub>2</sub> absorption isotherms. (e) In situ FTIR spectra for the adsorption and activation of CO<sub>2</sub> on HCNT-NA sample. (f) Gibbs free energy diagram for photoreduction of CO<sub>2</sub> to CO on BCN and HCNT-NA. Charge difference of CO<sub>2</sub> absorbed on (g) BCN and (h) HCNT-NA.



**Fig. 4.** Femtosecond transient absorption spectroscopy of BCN and HCNT-NA (a) Color plot of TA spectra for BCN and HCN-NA (b). (c) The TA spectrum of BCN and HCNT-NA after 400 nm excitation at zero delay time (d) carrier dynamics of BCN and HCNT-NA substrated from the ground state bleach signal.

Journal of Materials Chemistry A Accepted Manuscript

### **Table of Contents Entry**

View Article Online DOI: 10.1039/D0TA03870A

The edge-activation of polymeric carbon nitride matrix by hydroxyethyl group,

allowing enhanced  $CO_2$  absorption capacity, lowered  $CO_2$  activation energy barrier.

