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# Ultrathin Porous Carbon Nitride Bundles with an Adjustable Energy Band Structure toward Simultaneous Solar Photocatalytic Water Splitting and Selective Phenylcarbinol Oxidation

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Abstract: Rational design of photocatalysts with multiple functions, including organic synthesis and water-splitting, is promising and challenging. Herein, we synthesized actiniae-like carbon nitride (ACN) bundles based on the pyrolysis of an asymmetric supramolecular precursor prepared from L-arginine (L-Arg) and melamine. ACN has adjustable band gaps (2.25 eV  $\sim$  2.75 eV) and hollow microtubes with ultrathin pore walls, which enrich reaction sites, improve visible-light absorption and enhance charge separation. In the presence of phenylcarbinol, ACN exhibited excellent water-splitting ability (95.3 µmol/h) and in the meanwhile phenylcarbinol was selectively oxidized to benzaldehyde (conversion of 90.9 %, selectivity of 99.7 %) under solar irradiation. For the concurrent reactions, <sup>2</sup>D isotope labeling, separation and detection were conducted to confirm that the proton source of released hydrogen is water. Further, we theorize the mechanism of water splitting and phenylcarbinol oxidation and hope that it provides inspiration for simultaneous utilization of photogenerated electrons and holes in one system.

#### Introduction

As is well known, the conversion of sunlight into chemical energy is an important and promising clean energy technology.<sup>[1]</sup> For instance, water splitting triggered by a photocatalyst can produce hydrogen, which has become a popular substitute for fossil fuels.<sup>[2]</sup> The synthesis of high value-added products by selective photocatalytic organic oxidation, especially the synthesis of aldehydes by selective oxidation of alcohols, is also an interesting research direction.[3] An efficient solar photocatalyst needs to have a proper band gap, stable molecular structure,<sup>[1]</sup> and rapid charge dynamics.<sup>[4]</sup> Graphitic carbon nitride (CN) as an organic semiconductor photocatalyst has exhibited great potential for photocatalytic hydrogen evolution and selective oxidation because of its appealing thermal and chemical stability, nontoxicity to the environment, facile synthesis, and appropriate band structure.[4d, 5] However, bulk graphitic carbon nitride (BCN) still faces a variety of

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Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen, 518055, China Supporting information for this article is given via a link at the end of the document. problems, including low specific surface area, low utilization of visible-light, and severe recombination of photo-induced electron-hole pairs, which inhibit its wider application.<sup>[6]</sup> To solve these problems and optimize BCN's photocatalytic performance, many strategies have been explored, such as crystal structure engineering,<sup>[7]</sup> morphology control,<sup>[8]</sup> doping,<sup>[4e, 9]</sup> and composite structure design.<sup>[10]</sup>

Among these strategies, morphology control such as the creation of ultrathin or porous structure has been proven particularly effective.[11] Hard templating and physical/chemical exfoliation are common methods to prepare porous or ultrathin CN materials.<sup>[12]</sup> However, the former is time-consuming and the latter is restricted by low yields. Moreover, accurate tuning of the morphology and the energy band structure simultaneously is difficult to achieve by using either method. It is noteworthy that the formation of a supramolecular precursor via self-assembly is able to allow for the control of morphology and ingredient at the molecular level.<sup>[4d, 13]</sup> In our previous work, CN with ordered and hollow structure was synthesized from cyanuric acid-melamine supramolecular complexes, and it had great photocatalytic hydrogen evolution activity under visible-light irradiation.<sup>[14]</sup> Furthermore, after a sequential process of glycol molecules intercalation, thermal-induced condensation and exfoliation, supramolecular precursors could be converted into porous ultrathin CN nanosheets.<sup>[15]</sup> We found the change of C/N ratio is also important for the control of CN's energy band structure. Therefore, the introduction of molecular modules with different C/N ratios into a supramolecular precursor is a promising strategy for further enhancing the photocatalytic activity. Fortunately, amino acids have multiple special groups such as amino or carboxyl, which are potential supramolecular assembly modules. Furthermore, amino acids have different C/N ratios compared to melamine, which can be used for controlling the C/N ratio of the resultant supramolecular precursor. Meanwhile, the asymmetric feature of amino acid molecules can also be maintained and transferred to the final products.<sup>[16]</sup> Therefore, by use of the asymmetric amino acids-derived supramolecular precursor, the energy band structure and active sites of CN can be tuned, which are important factors for its catalytic performance.<sup>[4d]</sup>

Herein, L-Arg, a common amino acid, is used as an ingredient in the hydrothermal synthesis. As a Lewis base, the primary amino located at  $\alpha$ -carbon and the guanidine group cause the aqueous solution to be alkaline. Under this condition, melamine undergoes hydrolysis reaction to produce cyanic acid. Meanwhile, L-Arg bonds with melamine and cyanuric acid through the amidation reaction, forming a unique asymmetric supramolecular precursor (L-ArgM14) (Scheme 1a).

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Scheme 1. (a) Amidation reaction and assembly process between L-Arg, melamine and cyanuric acid during hydrothermal processes. L-Arg, a Lewis base, its guanidine group causes the aqueous solution to be alkaline, and so the melamine undergoes hydrolysis reaction to produce cyanic acid. Meanwhile, L-Arg could bond with melamine and cyanuric acid based on the amidation reaction to form a unique asymmetric supramolecular precursor. (b) The ultrathin porous ACN assembly can be obtained by the thermal condensation of supramolecular precursor. (c) The molecular structure of the final product (ACN).

After subjecting the supramolecular precursor to calcination, actiniae- like carbon nitride (ACN) assembled from a large number of tubular structures with ultrathin porous walls was obtained (Scheme 1b, 1c). Aromatic amino acids can interact with melamine molecules to form one-dimensional symmetric crystalline structures as described in the previous works.[17] In this work, we found that L-Arg can affect the growth process of the precursor and give rise to ACN with asymmetric topography morphologies and tunable band gaps. In addition, ordered tubular assemblies instead of random agglomeration of ultrathin structures, contribute to a large specific surface area of ACN, implying the accessibility of plenty of reaction sites that is helpful for achieving fast photocatalytic efficiency and durability of catalytic efficiency. The introduction of new carbon/oxygencontaining functional groups makes ACN14 very amphiphilic. By adjusting the C/N ratio, we obtained ACN with an appropriate band gap and band positions. In an aqueous solution using phenylcarbinol (PhCH<sub>2</sub>OH) as the hole scavenger, photocatalytic water splitting and selective oxidation of PhCH<sub>2</sub>OH to benzaldehyde (PhCHO) were realized simultaneously.

#### **Results and Discussion**

Melamine and L-Arg formed a supramolecular precursor (L-ArgM) of carbon nitrogen under the hydrothermal process. The

scanning electron microscopy (SEM, Figure 1a, b) images exhibit L-ArgM14 is composed of bundles of hollow tentacle-like structures, which have lengths of dozens of micrometers and orderly arrange on the core. By adjusting the L-Arg content and hydrothermal time, L-ArgM underwent a structural change (Figure S1, Figure S2). X-ray diffraction (XRD) experiments indicate that interactions between L-Arg and melamine occurred during the hydrothermal process and gave rise to a new structure (Figure S3). Meanwhile, the diffraction peaks for L-ArgM14 match quite well with melamine-cyanurate prepared by reacting melamine with cyanuric acid (Figure S4).<sup>[18]</sup> Cyanuric acid was produced due to the hydrolysis of melamine under the alkaline condition. However, an additional peak at 21.4° can be seen, which suggests the existence of a new set of lattice planes likely belonging to L-Arg in L-ArgM14.

Intermolecular hydrogen bonding was investigated by <sup>13</sup>C solid-state NMR (Figure 1c). There are double signal peaks at 167.5 and 169.1 ppm (I) with an intensity ratio of 2:1 for melamine. The non-equivalent property of carbon atoms was caused by varying strength of hydrogen bonding within melamine crystals.<sup>[19]</sup> While II and III corresponde to guanidine carbon and carboxyl carbon of L-Arg, respectively. Moreover, the signal peak of the carboxyl group is also cleaved, suggesting two matching modes arising from hydrogen bonding among carboxyl groups.

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Figure 1. SEM images of (a) L-ArgM14 and (b) a selected area in (a). (c) <sup>13</sup>C solid-state NMR of melamine, L-Arg and L-ArgM14. (d) SEM image of ACN14 (the inset is natural anemones). (e) TEM image of ACN14. (f) <sup>13</sup>C solid-state NMR spectra of ACN14 and BCN. (g), (h) C 1s and O1s XPS spectra of ACN14. (i) EELS spectra near carbon K-edge for BCN and ACN14.

Peaks II and III in the <sup>13</sup>C NMR spectrum of L-ArgM14 are consistent with that of arginine (Figure 1d), which indicates that the hydrogen bonding circumstances of guanidine and carboxyl in L-ArgM14 are similar to that of pure L-Arg. Guanidine bonds to atoms with lone pair electrons (O=, -N=), while carboxyl oxygen bonds with N-H. The peak VIII generally corresponds to carbon in cyanuric acid in the melamine-cyanuric acid system.<sup>[19]</sup> The asymmetry feature of peak VIII can be attributed to NH<sub>2</sub> released from the reaction between L-Arg carboxyl and melamine (Scheme 1a). Peak IV corresponds to melamine carbon in the melamine-cyanuric acid system. It is shifted by 2.0 ppm toward higher field relative to I because of the increase in the electron cloud density around the carbon atom based on the formation of N-H-O hydrogen bonds. The above results reveal that L-Arg reacted with melamine-cyanuric acid during the hydrothermal process to produce a special supramolecular precursor. Meanwhile, in the FT-IR spectra (Figure S5), the typical N-H of secondary amino stretching vibration peak at 3393 cm<sup>-1</sup> from amide can also be observed. The above conclusions are further confirmed by the Raman data (Figure S6). In addition, in-situ characterization method that combines

IR spectroscopy with thermogravimetric analysis (IR-TG) of L-ArgM14 manifest that the thermolysis temperature of L-ArgM14 (375 °C) is lower than that of pure melamine (425 °C) and the gas produced (HN=C=O) was the same (Figure S7, S8), indicating the formation of a new supramolecular structure. During the experimental procedure, after polymerization of precursor at 500 °C in N2, carbon nitride products were that have morphologies resembling svnthesized the corresponding precursors (Figure S9). The products consist of well-separated rod-shaped structures at low arginine content, and transformed to bundles and finally formed sea anemone-like assemblies as the content was increased. Photocatalytic hydrogen evolution results of series of ACNx indicate that ACN14 has the best performance (Figure S10), so ACN14 was used as typical product for the following measurements. Figure 1d is the SEM image of a representative ACN14 with a photo of sea anemones inserted. ACN14 is composed of a lot of tubes with lateral sizes between 1 and 3 µm (Figure 1d inset). TEM images further disclose these hollow structures (Figures 1e and S11a). The high-magnification TEM images of ACN14 exhibit that the ultrathin tube wall and the poriferous surface (Figure

Obviously, the crystal defects in the S11b, S11c). supramolecular precursors evolved into pores during thermal polymerization process. The specific surface area (SSA) is determined to be 171 m<sup>2</sup>/g, which is much higher than that of BCN (Figure S12 and S13). In addition, the pore volume of ACN14 is 0.75 m<sup>3</sup>/g, and the average pore diameter is 12.3 nm. The large SSA of ACN14 with a three-dimensional hierarchical structure is likely make ACN14 exposing a larger number of adsorption sites and reactive sites,[4d] which can prompt the adsorption of H<sub>2</sub>O, decrease the activation energy, and improve its durability of the catalytic performance in photocatalytic applications such as hydrogen evolution from water (Figure S14). The XRD pattern of ACN14 has two typical broad peaks at 13.3° and 27.0°, corresponding to the (100) and (002) lattice planes of graphitic carbon nitride, respectively (Figure S15).[4e, 20] This result is in line with the Raman spectrum of ACN14 that exhibits a G band lower than that of BCN (Figure S16).[21] The single peak at 810 cm<sup>-1</sup> and strong peaks at 1200~1600 cm<sup>-1</sup> in FT-IR prove that ACN14 contains the same structure unit of heptazine as BCN (Figure S17).<sup>[22]</sup>

The signals of <sup>13</sup>C solid state nuclear magnetic resonance (NMR) at 165 and 157 ppm (Figure 1f) confirm that heptazine is present in ACN14 and BCN.<sup>[15]</sup> In addition, the peak at 182 ppm corresponds to aldehyde groups that are directly attached to the carbon atoms in the CN heterocyclic rings of ACN14. The heptazine-conjugated structure causes the peak of aldehyde carbon nucleus to move toward a high field relative to the classical values.<sup>[23]</sup> The presence of aldehyde groups can greatly improve the water-adsorption rate and intramolecular polarization, which will enhance the photogenerated charge separation.<sup>[1d, 4b, c]</sup> The signal at 222 ppm stems from amorphous carbon. For carbon nitride, the peaks in the range of 60~100 ppm in the low field are mainly from amorphous carbon with sp sp<sup>2</sup>-hybridization and ether-based carbon with sp<sup>3</sup> or hybridization. The signal at about 23 ppm indicates the presence of sp<sup>3</sup>-hybridized carbon in ACN14. The introduction of carbon with weak polarity contributes to its lipophilicity.

The chemical state of BCN and ACN14's constituent elements were studied by X-ray photoelectron spectroscopy (XPS, Figure S18). ACN14's C 1s spectrum was deconvoluted into five peaks (Figure 1g) and BCN into four peaks. Peaks at the binding energies of 284.6, 285.9, 288.2 and 290.4 eV are respectively assigned to adventitious carbon, sp<sup>3</sup> carbon bonded to oxygen (C-O), sp<sup>2</sup>-hybridized carbon of triazine ring (N-C=N)<sup>[20]</sup> and the aldehyde carbon.<sup>[22]</sup> The deconvolution of N 1s spectrum resulted in four peaks at 398.6, 399.8 and 401.0 (Figure S18c, f), corresponding to sp<sup>2</sup>-hybridized nitrogen of triazine ring (C-N=C), bridging nitrogen (NC<sub>3</sub>) and amino nitrogen (e.g., -NH-, -NH<sub>2</sub>).<sup>[5b]</sup> Lastly, the peaks at 293.7 eV in C1s and 404.2 eV in N1s are attributable to the  $\pi$  electrons localization in the C<sub>3</sub>N<sub>3</sub> heterocycles. In the O 1s spectrum (Figure 1h, S118b, e), the peaks for sp<sup>3</sup> hybridized oxygens located at 531.4 eV (H<sub>2</sub>O) and 532.7 eV (C-O).<sup>[9c]</sup> The peak at 533.8 eV is attributed to sp<sup>2</sup> hybridized aldehyde oxygen.[22] This reveals that the main skeleton of ACN14 is consistent with that of BCN, and the aldehyde group conjugated with the main skeleton of CN is

introduced. Table S1 and Table S2 exhibit that ACN14's carbon and oxygen contents are higher than that of BCN.

The electron energy-loss (EELS) spectra of ACN14 and BCN present peaks arising from  $\pi^*$  and  $\sigma^*$  resonances near the K-edges of C and N (Figure S19). C K-edges of ACN14 are located at 287.25 and 298.25 eV, which correspond to 1s- $\pi^*$  and 1s- $\sigma^*$  electron transitions for sp<sup>2</sup>-hybridized carbon, respectively (Figure 1i).<sup>[2a, 9d, 24]</sup> Moreover, the C K-edge of ACN14 is shifted about 1 eV toward higher energies than that of BCN due to the presence of aldehyde oxygen that reduces heptazine-electron density. In addition, ACN14 has a larger area ratio of peak  $\pi^*$  to peak  $\sigma^*$  ( $\pi^*/\sigma^*$ ) than BCN does, indicating that ACN14 has a higher conjugate degree than BCN,<sup>[25]</sup>. The N K-edges are also listed as Figure S20.

In order to gain a deep understanding of ACN14 catalyst, firstprinciple calculation based on the density functional theory (DFT) was carried out. For BCN, the results of energy band structure and density of state (DOS) indicate that both C 2p and N 2p orbitals contributed to the conduction band (CB) while the valence band (VB) mainly is composed of N 2p orbitals (Figure 2a, 2b), which is in agreement with the literature.<sup>[26]</sup> According to the structural analysis of ACN14, the aldehyde groups have been introduced into the unit cell of melon-based carbon nitride to substitute the amino groups (Figure 2c). The calculation results of band structure and DOS indicated that both C 2p and N 2p orbitals contribute to the CB while the VB mainly consist of N 2p orbitals with some mixture of C 2p and O 2p for ACN14 (Figure 2d).<sup>[27]</sup> Furthermore, the modification of aldehyde will generate some new energy states, which arise from hybridization of N 2p, C 2p, and O 2p orbitals within the CB and VB of ACN14 (Figure 2d). Whereby, the electron transfer from N 2p states to CB during photoexcitation process will be improved. The results imply that introducing aldehyde groups to the edge of heptazine ring in carbon nitride may be a feasible strategy to narrow the energy band and improve the visible-light absorption.

The absorption spectrum of ACN14 obtained by UV-vis diffuse reflectance spectroscopy (DRS) exhibits higher absorption than that of BCN in the wavelength range except for 370 ~ 450 nm (Figure 2e). Generally, the introduction of oxygen-containing functional groups,<sup>[28]</sup> extra carbon atoms,<sup>[26, 29]</sup> lower crystallinity<sup>[7b, 30]</sup> and higher conjugation<sup>[31]</sup> can lead to red shift of the intrinsic absorption edge of graphite carbon nitride. Interestingly, in addition to intrinsic absorption, ACN14 has strong absorption in the infrared region, which make it has the capacity of photocatalytic hydrogen evolution in red light range under sacrifice reagent triethanolamine (8.11 µmol/h at 650 nm, 7.34 µmol/h at 700 nm, Figure S21). which can be attributed to the abundant intermediate energy levels in the band gap. And the apparent quantum efficiency (AQE) and solar-to-hydrogen (STH) at the wavelength of 420nm reach 9.2% and 3.8% respectively. Evident from similar dependence of PHE rate, AQE and DRS indicates hydrogen evolution induced by ACN14 truly proceeds via a photocatalytic mechanism (Figure S22). The band gap of ACN14 is about 2.56 eV, which is smaller than that of BCN (2.75 eV) (Figure S23), confirming the rationality of the theoretical calculation parameters and results.

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Figure 2. (a), (c) Optimized structure of BCN and ACN14. (b), (d) calculated band structure and corresponding density of state (DOS) of BCN and ACN14; (e) DRS absorption spectra and (f) the corresponding band gap values; (g) Band positions of ACN14 and BCN with the change of C/N ratio.

Meanwhile, the absorption line can be extended to the X-axis and the resultant intercept is about 1.0 eV as exhibited in the inset. So, the absorption wavelength range can cover infrared light. Usually for graphitic carbon nitride,  $n \rightarrow \pi^*$  transition can lead to this special DRS absorption tail.

Elemental analysis reveals different C/N ratios of the ACNx (x stands for the molar percentage of L-Arg to melamine and is in the range from 1 to 100) samples (Table S3). With the increase of arginine, the amount of carbon in ACNx was increased, which may be caused by the increase in polymerization degree. The proper C/N ratio is the key for the photocatalytic performance. In addition, the band gaps gradually decrease from 2.75 eV for BCN to 2.25 eV for ACN100 with the gradual increase in the L-Arg dosage (Figure S24). Therefore, the change trend of the band gap is inversely proportional to C/N of these samples. It is very interesting that with the increase in C/N, both the VB top and CB bottom of the sample falls first and then rises, and the lowest point occurs for ACN14 (Figure 2f). The band structures, determined from the band gap values and VB positions (Figure S25) of the samples, indicate that all the samples are thermodynamically capable of photocatalytic hydrogen evolution. This indicates that, as an n-type semiconductor, ACNx has a higher concentration of free electrons in the CB than BCN, which is beneficial to electron transport in the semiconductor. Although the reduction capacity of ACN14's CB is weak, higher hydrogen evolution efficiency with platinum as co-catalyst was still

achieved. It is due to the enhanced electron transfer kinetics, which makes up for thermodynamic disadvantages. The flat band potentials of these samples obtained from Mott-Schottky plots confirm this conclusion (Figure S26, S27).



Figure 3. (a) TR-PL of BCN and ACN; (b) Steady-state PL spectra of ACN14 and BCN; (c) TS-SPV spectra of ACN14 and BCN; (d) Electron paramagnetic resonance (EPR) of BCN and ACN14.

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**Figure 4.** (a) Photocatalytic pure water splitting for  $H_2$  evolution efficiency of BCN-1% and ACN14-0.1%, 1.0%, 2.0%. (b) Time course of  $H_2$  production (left axis) and evolution efficiency (right axis) for ACN14-1%. (c) EPR detection of in-situ formed EMPO-•O<sub>2</sub> for ACN14 in methanol. (d) PhCHO and  $H_2$  evolution efficiency, (e) conversion and selection of PhCHO evolution after 12 h of solar irradiation and (f) reaction mechanism of solar photocatalytic water-splitting and PhCH<sub>2</sub>OH-oxidation for BCN-1%, ACN14-0.1%, 1.0%, 2.0%.

Time-resolved photoluminescence (TR-PL) spectroscopy was used to study the transport and quenching mechanism of photogenerated excitons (Figure 3a). The average fluorescence lifetime for ACN14 (19.2 ns) is much smaller than that for BCN (53.12 ns). Moreover, all three positive decay components (T1, T2 and T3) for ACN14 are smaller than those for BCN. In general, T1, T2 and T3 reflect the rates at which photogenerated electrons in the sample fall from  $\sigma^*$ ,  $\pi^*$  and intermediate trap states to the ground state respectively.<sup>[24, 32]</sup> Thus, ACN14 has a faster rate of non-radiative recombination of photogenerated charge carriers and therefore larger charge mobility than BCN.<sup>[9c]</sup> The fractional intensity of T2 for ACN14 is 41.54%, higher than that for of BCN (31.29 %, inset of Figure 3a), indicating that the excited electrons in this ACN14 mainly exists in the  $\pi^*$ , which suggests that it has a stronger  $\pi$  conjugate system based on the aldehyde than BCN.<sup>[33]</sup> The steady-state photoluminescence (PL) spectrum of ACN14 exhibits negligible emission, much weaker than that of BCN, indicating that the charge carriers in ACN14 have very low probability of undergoing radiative recombination (Figure 3b).[1d, 4a, d]

The transient-state (TS) surface photovoltage (SPV) spectra of ACN14 and BCN were measured (Figure 3c) to explore the dynamical processes of photogenerated charge carriers. In rapid response range, ACN14 exhibit high photovoltage signal, and BCN has weak response signal. This indicates that the separation of electron-hole pairs is more efficient for ACN14 due to its stronger built-in electric field. <sup>[4a]</sup> In the range of >10<sup>-4</sup> s,

ACN's photovoltage signal is about 5 times stronger than that of BCN, suggesting that the photogenerated charge carriers in ACN transport more quickly from the bulk to the surface.

In Figure 3d, the Lorentz lines of both samples present a single resonance peak at a g value of 2.003, which is assigned to unpaired electrons of sp<sup>2</sup>-hybridized carbon atoms in the conjugated aromatic ring.<sup>[4d, 8a, 34]</sup> ACN14 has stronger peak intensity than BCN, which indicates that the electron density of ACN's CB is much larger than that of BCN.

We found that band adjustment gave ACNx new photocatalytic capability; highly efficient hydrogen evolution (up to 16.4 µmol/h) and H<sub>2</sub>O<sub>2</sub> were achieved by ACN14-1.0% in photocatalytic overall pure water-splitting at 25 °C (Figure 4a, Figure S28, Table S4). It is much higher than that of BCN-1% (4.49 µmol/h) prepared under the same condition. With the extension of irradiation time, hydrogen evolution efficiency slowly declined (Figure 4b). Moreover, the hydrogen evolution performance of ACN14-2% is far lower than that of ACN14-1%. (Figure S29). The EPR results in Figure 4c indicate that the VB of ACN14 can produce superoxide radical (•O2) in methanol under light with oxygen.[3a, 35] Therefore, the 4e-2e- pathway may occur in the production of H<sub>2</sub>O<sub>2</sub> from pure water-splitting under vacuum conditions (Figure S30).<sup>[36]</sup> Under the same condition, ACN14 can produce stronger Lorentz signal than BCN (Figure S31), indicating that ACN14 produced more photoinduced electrons.[4d]

The slow water oxidation reaction, which is the ratedetermining step, limits the hydrogen evolution efficiency of photocatalytic overall water-splitting.<sup>[1b, 4a, 35]</sup> Dehydrogenation of PhCH<sub>2</sub>OH (2 e<sup>-</sup> process) is kinetically more favorable than water oxidation (4 e<sup>-</sup> process)<sup>[37]</sup>. We used PhCH<sub>2</sub>OH as the wateroxidation promoter to achieve both water-splitting and selective PhCH<sub>2</sub>OH oxidation. After platinum (0.1wt%, 1wt%, 2wt%) was deposited on ACN14 under freezing conditions, highly efficient photocatalytic hydrogen evolution and PhCH<sub>2</sub>OH oxidation were achieved in water and PhCH<sub>2</sub>OH under solar irradiation at 25 °C (Table S4, entry 3, 4, 5). ACN14-1% exhibits the highest efficiency of PhCH<sub>2</sub>OH oxidation to produce PhCHO (conversion/90.9%; selectivity/99.7%) and hydrogen evolution efficiency (95.3 µmol/h/20 mg) (Figure 4d, e). Importantly, in the simultaneous reactions of water-splitting and PhCH<sub>2</sub>OHoxidation over ACN14-1%, the hydrogen evolution was markedly improved compared to that in ultrapure water; however, this improvement was not observed for BCN-1% (Table S4). The hydrogen evolution for ACN14-1% in the emulsion was 5.8 times higher than that in pure water. ESR results indicate that ACN14-1% only produced  $\cdot O_2^-$  under irradiation, but BCN-1% released a small quantity of •OH (Figure S32). Above results indicate that the collaboration between photocatalytic water-splitting and PhCH<sub>2</sub>OH oxidation greatly promotes each of the individual reaction. Time-extended experiments verified that the emulsion could keep producing hydrogen when PhCH<sub>2</sub>OH was exhausted (Figure S33), although the hydrogen evolution efficiency declined significantly with the reduction of PhCH<sub>2</sub>OH (Figure S34).

To verify the proton source of produced hydrogen <sup>2</sup>D isotope labeling photocatalytic experiments were carried out. ACN14-1% cannot catalyze deuterium water (D<sub>2</sub>O) splitting to give deuterium (D<sub>2</sub>) under solar irradiation (Figure S35b) because deuterium's heavier atomic mass reduces its chemical reactivity.<sup>[3b]</sup> When D<sub>2</sub>O instead of H<sub>2</sub>O was mixed with PhCH<sub>2</sub>OH, the splitting of water was blocked (Figure S35c). In the combination of H<sub>2</sub>O and PhCD<sub>2</sub>OH, H<sub>2</sub> was the only product, no D<sub>2</sub> or HD was detected (Figure S35d), which further confirms that the proton of H<sub>2</sub> is from water.

Based on the above results, an attractive photocatalytic reaction mechanism was proposed (Figure 4f). In this photocatalytic coupling reaction, photoelectrons are transferred from the CB of ACN14 through platinum atoms (Pt) to water, reducing proton to generate H<sub>2</sub>. At the same time, holes in ACN14's VB oxidize water to get oxygen-active species  $\cdot O_2^{-}$  and release H<sup>+</sup>. Finally, on the surface of ACN14, PhCH<sub>2</sub>OH react with  $\cdot O_2^{-}$  generated to form PhCHO. Meanwhile, part proton in system could combine  $\cdot O^{2-}$  to form H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> and  $\cdot O^{2-}$  will be consumed for the oxidation of PhCH<sub>2</sub>OH. The two reactions were coupled with each other, and the efficient photocatalytic oxidation and reduction were realized simultaneously.

#### Conclusion

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Due to amidation reaction, L-Arg can induce the hydrolysis and the assembly of melamine to form an asymmetric supramolecular precursor, which after undergoing thermalinduced polymerization resulted in hierarchically anemones-like carbon nitride (ACN14) with ultrathin porous walls. The C/N ratio and the band gap structure of ACN14 are adjustable from 2.75 eV to 2.25 eV, and it has abundant aldehyde groups and pores. The concurrent reactions of water-splitting and PhCH2OH oxidation were carried out in an emulsion of water and PhCH<sub>2</sub>OH with ACN14-1% (20 mg), which resulted in high hydrogen evolution efficiency (95.3 µmol/h), large PhCH<sub>2</sub>OH conversion rate (90.9%) as well as high PhCHO selectivity (99.7%). <sup>2</sup>D labeling results indicate that the protons of released hydrogen mainly come from water. This work demonstrates that the introduction of amino acid during the synthesis can change the elemental composition, energy band structure and morphology of CN, which in turn can enhance its thermodynamic and dynamical properties in photocatalytic processes.

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**Keywords:** Supramolecular assembly • Carbon nitride • Photocatalysis • Water splitting • Phenylcarbinol oxidation

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### **RESEARCH ARTICLE**

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### **RESEARCH ARTICLE**

Ultrathin porous carbon nitride bundles with adjustable energy band were designed based on the pyrolysis of asymmetric supramolecular precursor from L-arginine and melamine. It had high specific surface area, adjustable band gap. Through the coupling of water-splitting and phenylcarbinol oxidation, the efficiency of hydrogen evolution was promoted and phenylcarbinol oxidation was activated, which realized the synchronous and efficient utilization of photoelectrons and holes.



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Ultrathin Porous Carbon Nitride Bundles with an Adjustable Energy Band Structure toward Simultaneous Solar Photocatalytic Water Splitting and Selective Phenylcarbinol Oxidation