Optimizing the Crystallization Process of Conjugated Polymer Photocatalysts to Promote Electron Transfer and Molecular Oxygen Activation

Wei Ren, Jiajia Cheng, Honghui Ou, Caijin Huang, Masakazu Anpo, Xinchen Wang

PII:	S0021-9517(20)30279-7		
DOI:	https://doi.org/10.1016/j.jcat.2020.07.005		
Reference:	YJCAT 13817		
To appear in:	Journal of Catalysis		
Received Date:	1 June 2020		
Revised Date:	3 July 2020		
Accepted Date:	4 July 2020		



Please cite this article as: W. Ren, J. Cheng, H. Ou, C. Huang, M. Anpo, X. Wang, Optimizing the Crystallization Process of Conjugated Polymer Photocatalysts to Promote Electron Transfer and Molecular Oxygen Activation, *Journal of Catalysis* (2020), doi: https://doi.org/10.1016/j.jcat.2020.07.005

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Inc.

## **Optimizing the Crystallization Process of Conjugated Polymer Photocatalysts**

## to Promote Electron Transfer and Molecular Oxygen Activation

Wei Ren, Jiajia Cheng,\* Honghui Ou, Caijin Huang, Masakazu Anpo\* and Xinchen Wang\* State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, P. R. China, <u>http://wanglab.fzu.edu.cn</u>.

E-mail: xcwang@fzu.edu.cn; anpo@chem.osakafu-u.ac.jp; jjcheng@fzu.edu.cn.

This article is dedicated to, and in memory of, the late Prof. Michel CHE.

Abstract: Photocatalytic reactive oxygen species (ROS)-induced reactions provide an appealing method to solve the environmental and energy issues, whereas the current oxidation reaction generally suffered from low efficiency and poor selectivity due to uncontrollable  $O_2$  activation process. In view of the existence of competitive electron and energy transfer pathway, we propose that highly efficient superoxide radical anion ( $\cdot O_2^-$ ) generation can be achieved by optimizing the order degree of the photocatalyst. Herein, by taking carbon nitride polymer as an example, we optimized the crystallization process of carbon nitride polymer by selecting precursors of different polymerization degrees with a molten salt method. Benefiting from the high crystallinity, extended  $\pi$ -conjugated system and strong van der-Waals interactions between interlayers, the modified carbon nitride polymer exhibited accelerated charge transport and enhancement in electron induced molecular oxygen activation reactions under visible light. Consequently, the CCN-P exhibits about 1.5 times higher conversion rate in hydroxylation of phenylboronic acid and over 6-fold faster degradation rate in Rh B organic pollutants photodegradation with respect to pristine carbon nitride. This study provides an in-depth

understanding on the optimization of the  $O_2$  activation process and the design of advanced photocatalysts.

**Key words**: Crystalline carbon nitride, molecular oxygen activation, photocatalysis, electron transfer, reactive oxygen species

2

#### 1. Introduction

The selective oxygenation of organic compounds is widely recognized as one of the most important processes both in the laboratory and industrial synthetic chemistry [1-3]. While due to the usually high oxidation potential of the substrates, most oxidation strategies concentrated on the chemical process at high pressure and temperature, resulting in excessive energy consumption and environmental pollution [4-7]. Moreover, expensive noble-metal catalysts and hazardous stoichiometric oxidants have been employed, and the formation of undesired side products usually leads to the troublesome product purification process [8-10]. Therefore, developing greener reaction pathway for surmounting the energetic barrier of selective oxygenation reactions is highly desired.

Photocatalysis that directly harvests clean and renewable solar energy provides an appealing strategy to resolve the above problems under green and mild conditions [11-13]. In general, the ground state triplet molecular oxygen is forbidden to react with singlet organic molecules by Wigner's spin selection rule [14]. Fortunately, photocatalytic activation of molecular oxygen can be realized via the electron or energy-transfer pathway from photocatalyst to  $O_2$  [15, 16]. Specifically, reactive oxygen species (ROS), such as superoxide radical anion ( $\cdot O_2^{-}$ ), hydroxyl radical ( $\cdot OH$ ) and hydrogen peroxide ( $H_2O_2$ ), can be produced by transferring photogenerated electrons from the surface of semiconductors to oxygen molecules. On the other hand, energy transfer from the excited state of photo-sensitizer produces highly active singlet oxygen ( $^{1}O_2$ ) [17, 18]. Different oxidizing abilities were observed with various ROS. The development of photocatalyzed controllable  $O_2$  activation processes to achieve efficient ROS generation is therefore required for the sustainable oxidation chemistry. Superoxide radical anion ( $\cdot O_2^{-}$ ), a typical charge transfer activated ROS, has been widely used as a mild and green oxidant in the organic

transformations [19, 20]. For example, the photocatalyzed aerobic oxidative hydroxylation of arylboronic acid to substituted phenol, a versatile intermediate and important building block in the chemical and pharmaceutical industry, closely related to the generation of superoxide radical anion [21]. Therefore, due to the existence of competitive electron and energy transfer pathway, efficient electron transfer from the catalyst to the molecular  $O_2$  was essential to realize the selective superoxide radical anion generation [22].

Benefiting from its peculiar physicochemical properties, high stability and moderate band gap, the organic conjugated polymer has been widely employed in various photocatalytic reactions using visible spectrum [23-26]. Nonetheless due to the blocked charge carrier transfer in the amorphous conjugated polymer semiconductors,  $\cdot O_2^-$  evolution in general suffers from low level of efficiency [27-28]. The electron transport in photocatalysts is closely related to the order degree of the structures [29-31]. Accordingly, modulating the order degree of the semiconductor structure can promote photogenerated charge carrier mobility and optimize the electron transport. Consequently, the separation and transfer kinetics of photogenerated charges is accelerated, and high-efficiency ROS generation could be anticipated. As a metal-free visible light photocatalyst, the melon-based carbon nitride polymer (PCN) has attracted considerable attention during the past few years [32-34]. The pristine CN synthesized by conventional thermal polymerization of nitrogen containing precursors usually display an amorphous/semi-crystalline 2D layered morphology, which provided an ideal model to study the influence of the order degree on the charge transport and further on the  $O_2$  activation process [35-37]. Recently, the use of molten salt as the solvent and template has been recognized as a feasible way to promote the polymerization and further tailor the structure and properties of the semiconductor [38-40]. To that end, we are encouraged to construct highly ordered carbon nitride with molten salt and optimize the crystallization process of carbon nitride polymer to boost electron transfer for the efficient molecular oxygen activation.

Herein, two different polymerization degrees of heptazine-based carbon nitride materials, melem-based oligomer and melon-based polymer (noted as PCN), were first synthesized via heating dicyandiamide molecules at different temperatures. After that, the heptazine-based carbon nitride polymers of varying crystallinity degrees (noted as CCN-O and CCN-P, respectively) were successfully obtained by the ionothermal synthesis of the preheated melembased oligomer and PCN polymer as the precursors (Scheme 1). It was found that the charge transfer was indeed modified and the resulting O2 activation process could be manipulated depending on the crystallinity degree of the polymer. Notably, the CCN-P sample, which contained the more extended  $\pi$ -conjugated system and tighter layer-to-layer stacks (Scheme 2), exhibits significant boosted photogenic carrier migration and superior photocatalytic performance in subsequent photocatalytic molecular oxygen activation experiments. Benefiting from its optimal structural characteristics, the promoted electron transfer-involved photocatalytic processes in carbon nitride semiconductors lead to the excellent conversion of phenylboronic acid with over 99% selectivity, as well as complete degradation of organic pollutants. Additionally, the CCN-P shows high stability during the prolonged photochemical cycle reaction. This work gives us an in-depth understanding for the optimization of the O<sub>2</sub> activation process and the design of efficient metal-free photocatalysts via crystal engineering.

#### 2. Experimental Section

**2.1. Preparation of precursors:** 8 g of dicyandiamide (DCDA) was placed into a porcelain crucible with a cover. Then it was thermal heated at 450 °C or 550 °C in the air for 4 hours with a

heating rate of 5 °C min<sup>-1</sup> (450 °C for oligomer, 550 °C for PCN polymer). The yield of oligomer was 56%, for PCN polymer was 49%.

**2.2. Preparation of CCN-O and CCN-P:** 600 mg of corresponding precursor (melem-based oligomer or PCN polymer) and a eutectic mixture of LiCl (45 wt. %, 2.7 g) and KCl (55 wt. %, 3.3 g) were ground together. The mixed powder was placed in a covered ark and transferred into a tube furnace and heated to 550 °C with nitrogen flow (200 mL min<sup>-1</sup>) of 12 °C min<sup>-1</sup>. After keeping the temperature for 4 hours, the tube furnace naturally cooled to room temperature. The yellow-green product was washed with distilled water to remove residual salt, and dried at 60 °C. The CCN polymers obtained from different precursor were marked as CCN-O (O= melem-based oligomer) and CCN-P (P= PCN polymer), respectively. The yield of CCN-O was 92%, for CCN-P is 98%.

**2.3. Photocatalytic hydroxylation of phenylboronic acid:** The photocatalytic hydroxylation of phenylboronic acid was carried out as following: Catalyst (10 mg) and phenylboronic acid (0.5mmol) was poured into the mixture solution with triethylamine (TEA, 1.5mmol) dissolved in the acetonitrile (3 mL). Then, the mixture was transferred into a 10 mL Pyrex glass bottle filled with pure oxygen at atmospheric pressure. The suspensions were irradiated by a blue LED lamp. After the reaction, the mixture was centrifuged to completely remove the catalyst particles. The filtered solution was analyzed by <sup>1</sup>H NMR spectrum using 1, 3, 5-Trimethoxybenzene as the internal standard.

**2.4.** Photodegradation of organic pollutants: The photodegradation of organic pollutants was carried out using rhodamine B (noted as Rh B) as example. 20 mg of photocatalyst was mixed with 80 mL Rh B solution (10<sup>-5</sup> mol L<sup>-1</sup>) and ultrasonic uniform. Before irradiation, the mixture was stirred in dark for 30 min to attain an adsorption-desorption equilibrium. After that, it was

exposed to irradiation using a 300 W Xe-arc lamp equipping with cutoff filters ( $\lambda \ge 420$  nm) under constant magnetic stirring at 300 rpm. At several minutes' intervals, a 1.5 mL aliquot was taken out and centrifuged to get the supernatant. The supernatant was detected by UV-vis spectroscopy at a wavelength of 554 nm. And C/C<sub>0</sub> represents the degradation percentage, where C<sub>0</sub> is the initial concentration of Rh B solution, and C represents the concentration at different irradiation time.

**2.5.** Photocatalysts Characterizations: X-ray diffraction patterns (XRD) were collected on a Bruker D8 Advance diffractometer with Cu K $\alpha$ 1 radiation ( $\lambda$ =1.5406 Å). The field emission scanning electron microscopy (SEM) was done on a Hitachi SU8010 microscope. Transmission electron microscopy (TEM) measurement was conducted on a FEI Tencai 20 microscope. The solid-state <sup>13</sup>C cross polarization (CP)/magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured on a Bruker Advance III 500 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo ESCALAB250 instrument with a monochromatized Al Ka line source (200 W). BET surface area was measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 3020. The Fourier transform infrared (FTIR) spectra were recorded on a BioRad FTS 6000 spectrometer. The UV-visible diffuse reflectance spectra (UV-vis DRS) of the powders were obtained on a Varian Cary 500 Scan UV-visible system. The photocurrent performance analysis and Photoelectrochemical measurements were conducted using a BioLogic VSP-300 electrochemical system with a threeelectrode cell: work electrode (photocatalyst-coated FTO), counter electrode (Pt), and reference electrode (Ag/AgCl). And Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.2 M) as electrolyte at +0.6 V bias potential vs. Ag/AgCl. Electron paramagnetic resonance (EPR) was carried out on a Bruker model A300 spectrometer (Bruker Instruments, Inc.).<sup>1</sup>H NMR spectrum was measured on a Bruker Advance spectrometer in the solvents indicated. The total organic carbon (TOC) values were determined using a Shimadzu TOC-Vcph total organic carbon analyzer.

#### 3. Results and discussion

The crystallinity and the layered-stacking mode of all the photocatalysts were firstly analyzed by powder XRD patterns. As displayed in Figure 1a, the pristine PCN presents the typical diffraction pattern of melon-based carbon nitride polymer, two domain peaks located at 13.1° and 27.6° corresponding to (100) in-plane repeating heptazine units and (002) interlayer stacking peak [41]. For CCNs, an evident shift and narrowing of the two peaks are observed, suggesting the enhanced periodicity and crystallinity of the samples. Specifically, the shift of the (100) peak of CCNs to the lower degree (8.1° for CCNs, 13.1° for PCN) could be attributed to the extended distance of the interplanar repeat unit, indicating a more complete polymerization of CCNs after molten salt treatment [42]. In contrast, the narrowed and intensified (002) peaks of CCNs was shifted to higher degree (Figure 1b, 28.4° for CCN-P, 28.2° for CCN-O, 27.6° for PCN), reflecting a more tightly stacked interlayer distance caused by the stronger  $\pi$ - $\pi$ interactions between the neighboring heptazine layers [43]. Furthermore, the CCN-P constructed from melon-based PCN polymer exhibits shorter interlayer distance than CCN-O (constructed from melem-based oligomer), suggesting that the convergence degree of the precursor may have an impact on the crystallization process. HR-TEM (Figure 1c) further offers an intuitive observation for the crystallinity and interlayer stacking distance of the CCNs. In comparison with the pristine PCN sample (Figure S1), the clear two lattice fringes are observed on both CCNs. The measured lattice distances corresponding to 0.31 nm for CCN-O, 0.28 nm for CCN-P likely originated from the (002) interlayer space, and the other corresponding to 0.93 nm for CCN-O, 0.94 nm for CCN-P, which may be assigned as the (100) in-plane periodicity. The distances of

these lattice fringes are consistent with the XRD results. Combining with the above results, it clearly indicates that the obtained CCN samples show more extended  $\pi$ -conjugated system and more compact layer interaction than pristine carbon nitride. Especially, the CCN-P has tighter stacked layers than CCN-O. Those results also proved that the CCN-P constructed from melon-based PCN polymer is easy to form the more extended conjugated system than CCN-O which constructed from melem-based oligomer. Therefore, the extended in-plane conjugate system and decreased interlayer distance can significant promote the photoelectron transfer within the stacks and reduce the potential barrier on the surface, enhancing the photocatalytic performance accordingly [43].

The chemical structure of the CCNs was characterized at the molecular level by the solidstate <sup>13</sup>C CP-MAS NMR, FT-IR and XPS spectra. In the <sup>13</sup>C solid-state NMR patterns (**Figure 2a**), both CCN-O and CCN-P have two similar distinct responses for carbon species. The highintensity peak at 161.2 ppm could be attributed to the  $(NH_X)$ -CN<sub>2</sub> groups (C (e)) and the peak at 154.8 ppm corresponds to CN<sub>3</sub> groups (C (i)). The results confirmed that CCNs maintain the core structure of heptazines. In the FTIR spectra (**Figure 2b**), the characteristic peaks associated with the heptazine units are observed, such as the breathing modes located around 800 cm<sup>-1</sup> and the stretching vibration modes in the region of 1200-1700 cm<sup>-1</sup>. The distinct peaks of CCN samples reveal the promoted degree of polymerization and crystallinity degree. In addition to these retained absorption peaks, two new peaks located around 987 cm<sup>-1</sup> and 1151 cm<sup>-1</sup> are observed with the CCNs samples, which could be assigned to the symmetric and asymmetric vibrations of NC<sub>2</sub> bonds in metal-NC<sub>2</sub> groups, respectively (the presence of K could further be verified in the subsequent XPS measurement) [44]. And a new peak appears at around 2150 cm<sup>-1</sup>, is attributed to the typical cyano peak. This may connect with the defects in the re-condensation of terminal

ammonia group [45]. Obviously, the cyano peak intensity in CCN-P is lower than CCN-O, indicating more sufficient convergence of CCN-P compared with CCN-O.

The chemical state of the samples was further analyzed by the XPS measurements. As shown in Figure 2c, the C 1s spectrum of CCNs can be divided into peaks centered at 288.4 and 284.8 eV, attributed to the sp<sup>2</sup>-bonded carbon (-N-C=N) and the standard reference carbon. A new peak located at 286.4 eV can be assigned to the C species in cyano group (-C $\equiv$ N) [29]. Obviously, the area ratio of this peak in CCN-O is higher than in CCN-P (Table S1), which agrees well with FTIR result. The N 1s spectra of all samples (Figure 2d) can be resolved into four peaks which are assigned to the sp<sup>2</sup> hybridized N in C=N-C groups (398.8 eV), the tertiary N (-N-(C)<sub>3</sub>) in the center of heptazine units (400.1 eV), the N species in the terminal amino groups (401.2 eV), and the charging effects in heptazine units (404.6 eV), respectively [46]. Clearly, compared to PCN, the ratio of N species in terminal amino groups in CCN-O decrease to 8.6% and further minimized to 6.2% in CCN-P, suggesting the gradually enhanced polymerization degree (Table S2). Furthermore, none of Cl or Li species is introduced into the polymeric structure after LiCl/KCl salt melt treatment, except small amount of K ions was observed which may be used to neutralize a handful of terminal negative groups (Figure S2). On the basis of the above results, it can be concluded that the CCNs have the similar core chemical skeleton with amorphous PCN, while they exhibit much more complete polymerization and more tight stacked layers. Moreover, it is worth to mention that the higher degree of polymerization in the precursor, the higher crystallinity was observed in the obtained CCN samples. The morphological structure of the synthesized samples was implemented by SEM. As presented in Figure S3, the PCN exhibits a typical bulk-like morphology but CCNs exhibit a nanorod-shaped structure. Also notable is that the formation of nanorods is more complete in CCN-P than CCN-

O. This specific morphology of CCNs can efficiently increase the surface areas, which has been certified by the nitrogen absorption isotherms tests (**Figure S4**). The CCNs exhibited increased nitrogen adsorption capacity and pore volume. The BET surface area of CCN-P is 85 m<sup>2</sup>g<sup>-1</sup>, which is larger than CCN-O (59 m<sup>2</sup>g<sup>-1</sup>) and pristine CN (15 m<sup>2</sup>g<sup>-1</sup>).

The structure of the ordered plane and tight interlayer stacking is supposed to greatly affect charge carrier separation and transfer which play crucial factors in determining the photocatalytic performance. As the radiation decay of excitons leads to fluorescence, the optical excitation processes of CCNs were investigated by room temperature PL measurements [42]. In Figure 3a, the CCNs exhibit significant decreased emission intensity with respect to PCN, illustrating the greatly suppressed recombination of the photogenerated charges for CCNs. Moreover, timeresolved fluorescence spectra detected at the corresponding emission peaks give the mean radiative lifetime of 3.02 ns, 0.98 ns and 0.78 ns for PCN, CCN-O and CCN-P, respectively (Figure 3a, inset). The significantly reduced singlet excitons lifetime of CCN samples, clearly indicates the enhanced separation of photogenerated charge carriers. The PL quenching can be attributed to the optimized structural characteristics of CCNs for charge transfer, such as more unfolded intralayer structure, shorter interlayer distance, and lower surface defect density which mostly acting as charge recombination centers [29]. Furthermore, the transient photocurrent response (Figure 3b) shows about 1.5 times stronger photocurrent transient response of CCNs than that of the PCN. Meanwhile, as evidenced in Figure 3c, the electrochemical impedance spectroscopy (EIS) Nyquist plot of both CCNs exhibit a much smaller arc radius than that of PCN, which means the CCNs possess both lower electrochemical impedance and remarkably enhanced electron migration [47]. These results clearly indicate more efficient carrier separation and faster electron transfer on the surface of the obtained highly crystalline CCNs.

The optical absorptions of the polymers are investigated by the UV-vis DRS measurement. The **Figure S5a** shows that both CCNs display evident enhancement visible light absorption and a slight red-shift absorption edge than PCN. The band gaps of CCN-P and CCN-O determined according to the Tauc plot approach are 2.72 and 2.75 eV, respectively (**Figure S5c and S5d**), which are narrower than PCN (2.77 eV) (**Figure S5b**) [48]. The optimized optical absorption of CCNs would definitely benefit for the utilization of more incident photons in subsequent photoreaction [42]. The Mott-Schottky curves indicate typical n-type semiconductor behavior for all the samples. And the flat potential of CCN-P, CCN-O and PCN was determined to be -1.12V, -1.31V and -1.48 V vs Ag/AgCl (pH 6.6), respectively (**Figure S6**). In combination with their band gaps (**Figure 3d**), the CCNs and PCN exhibit appropriate CB (conduction band) and VB (valence band) positions that thermodynamic enable the rapid reduction of molecular oxygen.

By virtue of the promoted photogenic carrier migration and suitable band position, the CCNs are expected to be a promising photocatalyst for molecular oxygen activation reaction. Phenols serve as important building blocks in the chemical and pharmaceutical industries [49-51]. Photocatalytic oxidation of phenylboronic acid is an effective and direct method for the preparation of various substituted phenols [52-54]. Thus, the transformation of phenylboronic acid to phenol was selected as the model reaction to evaluate molecular oxygen activation capacity of the polymers. The PCN and CCNs photo-catalyzed hydroxylation of phenylboronic acid using triethylamine (Et<sub>3</sub>N) as the sacrificial reagent and molecular oxygen as the green oxidant was first investigated. The factors affecting this reaction were comprehensively explored through control experiments, and the results are listed in **Table 1**. The reaction takes place smoothly with either PCN or CCNs as the photocatalyst, resulting in the desired phenol product (entries 1-3). Obviously, phenylboronic acid was completely oxidized with CCN-P and the yield

(>99%) is about 1.5 times higher than that with PCN (68%). When  $N_2$  was used instead of  $O_2$ , almost no products could be detected (entry 4). This result clearly demonstrates that oxygen activation is the vital process for this reaction. In the absence of light, photocatalyst or Et<sub>3</sub>N, negligible conversion of phenylboronic acid was observed, indicating the key role of visible light, catalyst and amine in the reaction (entry 5-7).

To further verify the generality of the CCN catalyst for the aerobic oxidative hydroxylation, the electronic and steric effect of different substituents on aryl and alkyl boronic acid were investigated (Table 2). Obviously, bearing whatever the electron-deficient (entries 2-8) or electron-rich substituent on the phenyl moiety of the boronic acid (entry 9), the CCN-P always exhibited excellent photocatalytic performance (yield: > 90%). Besides, the substitution position on the benzene ring only had a little effect on the reaction outcome (entries 4 and 5). The disubstituted phenyl boronic acid, naphthylboronic acid has also been examined, and all of them are effectively converted into the corresponding phenol derivatives (entries 10 and 11). Furthermore, an alkylboronic acid was well tolerated under the optimal conditions and the corresponding product was obtained in satisfactory conversion (entry 12). To our delight, phenylboronic acid pinacol ester also proved to be a suitable candidate for the transformation (Figure 4, Eq. (1)). Moreover, with potassium phenyltrifluoroborate as the substrate, the reaction was able to convert completely into phenol after 12 h under the same reaction conditions as described above (Figure 4, Eq. (2)). Meanwhile, Figure S7 shows the catalytic cycle test with CCN-P as the photocatalyst. After four repeated cycles, no apparent deactivation in catalytic performance was observed, indicating the high stability of CCN-P during the prolonged photochemical reaction process. The high stability of the photo-catalyst is also demonstrated by the XRD patterns and FT-IR spectra for the used sample after the photo-reaction (Figure S9).

In order to explore the origin of oxygen in the product phenol, isotope labeling experiments is conducted. Excessive amounts of H<sub>2</sub><sup>18</sup>O was added to the system under the optimal reaction condition, and none of <sup>18</sup>O-labeled products were detected (Figure 4, Eq. (3)). This result indicated the oxygen atom in the product probably come from O<sub>2</sub>. Therefore, to investigate the main reactive oxygen species for inducing the photoreactions over CCN-P, the control experiments with p-benzoquinone (BQ), t-butyl alcohol (TBA), NaN<sub>3</sub>, catalase and KI employed as the corresponding •O2-, •OH, 1O2, H2O2 and h+ scavengers were performed. Figure 4a illustrates that the oxidation of phenylboronic acid is significantly inhibited in the presence of BQ or KI. However, there only caused a slight decrease in the reaction efficiency when TBA, NaN<sub>3</sub> or catalase was added to the reaction mixture. The results provided that the  $\cdot$ O<sub>2</sub><sup>-</sup> was the main oxygen-containing active species for the oxidation of phenylboronic acid in our system. Therefore, the generation of  $\cdot O_2^-$  over PCN and CCNs under visible-light irradiation was verified in an EPR spin-trapping experiment with DMPO at room-temperature. The EPR signal with a characteristic intensity ratio of 1:1:1:1 was observed, which is in line with that of DMPO- $\cdot$ O<sub>2</sub>adduct (Figure 4b). Additionally, the notable difference of the signal intensity of PCN and CCNs clearly confirm the enhanced  $\cdot O_2^-$  generation in CCNs system. Consistent with the conjugation and interlayer distance of their structures, the CCN-P presents stronger  $\cdot O_2$ -signals than CCN-O. The above results demonstrated that the  $\cdot O_2^-$  and  $h^+$  are the main active species in photooxidation of phenylboric acid with the CCN-P photocatalyst. The enhanced electron migration of CCN-P is beneficial for the generation of  $\cdot O_2^-$  during the photocatalytic molecular oxygen activation.

The photocatalytic molecular oxygen activation performance of the PCN and CCNs are further evaluated by the degradation of Rh B under visible light ( $\lambda \ge 420$  nm) irradiation. Before

the visible light illumination, all the samples are stirred for 30 minutes in dark to achieve the equilibrium of adsorption and desorption (**Figure S10**). After that, the photodegradation tests with PCN and CCNs were conducted. As displayed in **Figure 5a**, both CCN photocatalysts exhibit faster downtrend in Rh B concentrations than PCN polymer. As for CCN-P sample, after 60 minutes of visible light irradiation, over 94% of Rh B is photodegraded, while only 48% for pristine PCN. In contrast, when conducting this reaction without catalyst, no obvious change could be observed, indicating the stable nature of Rh B molecule. Furthermore, the mineralization rate by determining the total organic carbon (TOC) values was about 24.2% in the CCN/RhB system (**Figure S11**), suggesting that most of RhB was broken up into small molecules and harsher conditions may be required to realize the complete mineralization of RhB [55].

It is generally accepted that the photodegradation process of Rh B on the photocatalyst is indexed to the first-order kinetics with an equation as following ln (C<sub>0</sub>/C) = kt (k: Rate constant (min<sup>-1</sup>); C<sub>0</sub>: Initial concentration of Rh B; C: Actual concentration of Rh B) [18]. We have therefore calculated the rate constant k of PCN and CCNs to give a direct comparison of the photodegradation activity. As shown in **Figure 5b**, the k valves increased in the order of PCN (0.008 min<sup>-1</sup>), CCN-O (0.031 min<sup>-1</sup>) and CCN-P (0.050 min<sup>-1</sup>). The k value of CCN-P is shown to be more than 6 times higher than that of PCN, which is in accordance with the effective charge mobility across the compact layer-to-layer stacks and more conjugate planes. Moreover, CCN-P maintains the high degradation efficiency (over 90%) throughout three photocatalytic cycles (**Figure 5c**). When we pump N<sub>2</sub> into the reaction system to get the oxygen out of the air, the degrading rate of Rh B depresses clearly. It proved that the O<sub>2</sub> is essential for the degradation to proceed smoothly. Furthermore, when BQ was added into the system, the degradation rate was significantly inhibited, indicating the  $\cdot O_2^-$  is also playing key role in the photodegradation of Rh B over CCN-P (**Figure 5d**).

Based on the above studies, a proposed working mechanism for the hydroxylation of phenylboronic acid in CCN photocatalytic system is illustrated in **Scheme 3**. Briefly, the reaction starts with excitation of the photocatalyst CCN-P via irradiation, and single electron transfer (SET) from excited CCN-P to the molecular  $O_2$  leads to the formation of  $\bullet O_2^-$ . Subsequently, a peroxide radical intermediate was formed via reaction of the boronic acid (Ar-B(OH)<sub>2</sub>) with  $\bullet O_2^-$ , which undergo rearrangement and hydrolysis to deliver the final product [56]. In other hand, the photocatalyst CCN-P is regenerated in the presence of electron donor to close the photoredox cycle.

### 4. Conclusion

In summary, we have synthesized highly ordered carbon nitride by using precursors with different degrees of polymerization, which presented the advantages of the increased polymerization degree, more unfolded intralayer structure and shorter interlayer distance. The combination of fluorescence study, electrochemical analysis and EPR spectral observations demonstrated the significantly promoted photogenic carrier separation and transfer process, facilitating  $\cdot O_2^-$  evolution. Benefiting from the increased  $\cdot O_2^-$  production, the CCNs exhibit the superior activity in photocatalytic selective oxidations, including hydroxylation of phenylboronic acid and Rh B degradation. This study gives us an in-depth understanding on the advantages of CCN in molecular oxygen activation and a practical method to achieve more ROS-induced reactions by using CCN photocatalyst.



**Scheme 1**. Schematic diagram for synthesis of PCN, CCN-O and CCN-P from precursors with different polymerization degree (Dicyandiamide, Melem-based oligomer and Melon-based PCN polymer).

17



**Scheme 2.** Proposed interlayer charge carrier transfer of (left) pristine and (right) optimized CCN with shortened layer stacking distance.



Figure 1. The XRD patterns a) and enlarged XRD patterns b) of PCN and CCNs. c) TEM images of CCNs.



**Figure 2.** Solid-state <sup>13</sup>C CP-MAS NMR a), FTIR spectra b) and High-resolution XPS spectrum of c) C 1s and d) N 1s for PCN and CCNs.



**Figure 3.** a) Room temperature PL spectra of PCN and CCNs under 395 nm excitation. Inset: Time-resolved fluorescence kinetics monitored at the corresponding emission peaks of PCN and CCNs. Transient-state photocurrent response b) and Nyquist plots of electrochemical impedance spectroscopy c) of PCN and CCNs at +0.6 V *vs*. Ag/AgCl reference electrode using Pt as counter electrode. d) Schematic diagram showing the band structure of PCN, CCN-O and CCN-P versus Ag/AgCl, pH = 6.6.

B(OH) <sub>2</sub> Visible		light, Photocatalyst	
Et <sub>3</sub> N, MeCN, O <sub>2</sub>			
Entry <sup>a</sup>	Photocatalyst	Deviation from standard condition	Yield <sup>b</sup>
1	PCN	-	68
2	CCN-O	-	92
3	CCN-P		>99
4	CCN-P	N <sub>2</sub>	<1
5	CCN-P	No light	<1
6			6
7	CCN-P	No Et <sub>3</sub> N	<1

**Table 1**. Photocatalytic hydroxylation of arylboronic acids.

[a] Reaction conditions: phenylboronic acid (0.5 mmol), photocatalyst (10 mg),  $Et_3N$  (1.5 mmol), 3 mL CH<sub>3</sub>CN, and 1 atm O<sub>2</sub> for 4 h. [b] Determined by <sup>1</sup>H-NMR using 1,3,5-Trimethoxybenzene as an internal standard. MeCN = Acetonitrile.

**Table 2**. The oxidative hydroxylation of phenylboronic acid and alkenylboronic acid using

 CCN-P as the photocatalyst under standard conditions.



[a] Reaction conditions: phenylboronic acid (0.5 mmol), photocatalyst (10 mg), Et<sub>3</sub>N (1.5 mmol), 3 mL CH<sub>3</sub>CN, and 1 atm O<sub>2</sub> for 4 h. [b] Determined by <sup>1</sup>H-NMR using 1,3,5-Trimethoxybenzene as an internal standard.



**Figure 4.** a) Trapping experiments using active species scavengers (BQ, TBA, NaN<sub>3</sub>, catalase and KI employed as the corresponding  $\bullet O_2^-$ ,  $\bullet OH$ ,  $^1O_2$ ,  $H_2O_2$  and  $h^+$  scavengers) in phenylboronic acid hydroxylation for CCN-P. b) EPR spectra of DMPO- $\bullet O_2^-$  adducts in the system of PCN and CCNs under visible light irradiation.



**Figure 5.** a) Photocatalytic activities for Rh B degradation of PCN and CCNs. b) Relationship of degradation rate (k) and the light irradiation time for PCN and CCNs. c) Cycling runs for Rh B degradation in the presence of CCN-P sample. d) Effect of quencher additives on the photocatalytic activity of CCN-P in RhB degradation. BQ:  $\bullet O_2^-$  scavenger; KI: h<sup>+</sup> quencher.



Scheme 3. The proposed mechanism for the oxidation of phenylboronic acid in CCN-P photocatalytic system.

### **Conflicts of interest**

The authors declare no conflicts of interest.

Acknowledgment: This work was financially supported by the National Natural Science Foundation of China (U1905214, 21861130353, 21961142019, 21761132002 and 21425309), the Science Foundation of the Fujian Province (2019J01203), the National Key R&D Program of China (2018YFA0209301), the National Basic Research Program of China (2013CB632405), the Chang Jiang Scholars Program of China (T2016147) and the 111 Project (D16008).

### References

[1] K. Barta, P.C. Ford, Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids, Acc. Chem. Res. 47 (2014) 1503–1512.

[2] K. Zhao, L. Zhang, J. Wang, Q. Li, W. He, J.J. Yin, Surface Structure-Dependent Molecular Oxygen Activation of BiOCl Single-Crystalline Nanosheets, J. Am. Chem. Soc. 135 (2013) 15750-15753.

[3] Y. Liang, J. Wei, X. Qiu, N Jiao, Homogeneous Oxygenase Catalysis, Chem. Rev., 118 (2018) 4912–4945.

[4] X. Li, J. Chen, X. Wang, J. Sun, M. Antonietti, Metal-Free Activation of Dioxygen by Graphene/g-C<sub>3</sub>N<sub>4</sub> Nanocomposites: Functional Dyads for Selective Oxidation of Saturated Hydrocarbons, J. Am. Chem. Soc. 133 (2011) 8074–8077.

[5] X. Li, X. Wang, M. Antonietti, Solvent-Free and Metal-Free Oxidation of Toluene Using  $O_2$ and  $g-C_3N_4$  with Nanopores: Nanostructure Boosts the Catalytic Selectivity, ACS Catal. 2 (2012) 2082–2086.

[6] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, Recent advances in heterogeneous selective oxidation catalysis for sustainable chemistry, Chem. Soc. Rev, 43 (2014) 3480–3524.

[7] I. Hermans, E.S. Spier, U. Neuenschwander, N. Turra, A. Baiker, Selective oxidation catalysis: opportunities and challenges, Top. Catal. 52 (2009) 1162–1174.

[8] A.D. Chowdhury, S.M. Mobin, S. Mukherjee, S. Bhaduri, G.K. Lahiri, [Pd(L)Cl<sub>2</sub>]-Catalyzed Selective Hydroxylation of Arylboronic Acids to Phenols, Eur. J. Inorg. Chem. 2011, 3232–3239.
[9] L. Wang, W. Zhang, D.S. Su, X. Meng, F.S. Xiao, Supported Au nanoparticles as efficient catalysts for aerobic homocoupling of phenylboronic acid, Chem. Commun., 48 (2012) 5476–5478.

[10] K. Ji, J. Deng, H. Zang, J. Han, H. Arandiyan, H. Dai. Fabrication and high photocatalytic performance of noble metal nanoparticles supported on 3DOM InVO<sub>4</sub>–BiVO<sub>4</sub> for the visible-light-driven degradation of rhodamine B and methylene blue, Appl. Catal. B: Environ. 165 (2015) 285-295.

[11] C. Ayed, L.C.; Silva, D. Wang, K.A.I. Zhang, Designing conjugated microporous polymers for visible light promoted photocatalytic carbon-carbon double bond cleavage in aqueous medium, J. Mater. Chem. A, 6 (2018) 22145-22151.

[12] M. Zheng, T. Yuan, J. Shi, W. Cai, X. Wang, Photocatalytic Oxygenation and Deoxygenation Transformations over BCN Nanosheets, ACS Catal. 9 (2019) 8068–8072.

[13] N.S. Lewis, Research opportunities to advance solar energy utilization. Science 351 (2016) aad1920.

[14] C. Schweitzer, R. Schmidt, Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chem. Rev.* 103 (2003) 1685–1757. [15] M. Anpo, M. Che, B. Fubini, E. Garrone, E. Giamello, Paganini, M. C. Generation of superoxide ions at oxide surfaces, Top.Catal. 8 (1999) 189–198.

[16] H. Wang, S. Chen, D. Yong, X. Zhang, S. Li, W. Shao, X. Sun, B. Pan, Y. Xie, Giant Electron–Hole Interactions in Confined Layered Structures for Molecular Oxygen Activation, J. Am. Chem. Soc. 139 (2017) 4737–4742.

[17] H. Wang, S. Jiang, S. Chen, D. Li, X. Zhang, W. Shao, X. Sun, J. Xie, Z. Zhao, Q. Zhang, Y. Tian, Y. Xie, Enhanced Singlet Oxygen Generation in Oxidized Graphitic Carbon Nitride for Organic Synthesis, Adv. Mater. 28 (2016) 6940–6945.

[18] Y. Zheng, Z. Yu, H. Ou, A.M. Asiri, Y. Chen, X. Wang, Black Phosphorus and Polymeric Carbon Nitride Heterostructure for Photoinduced Molecular Oxygen Activation, Adv. Funct. Mater. 28 (2018) 1705407.

[19] X. Cao, Z. Chen, R. Lin, W. Cheong, S. Liu, J. Zhang, Q. Peng, C. Chen, T. Han, X. Tong,
Y. Wang, R. Shen, W. Zhu, D. Wang, Y. Li, A photochromic composite with enhanced carrier separation for the photocatalytic activation of benzylic C–H bonds in toluene, Nat. Catal., 1 (2018) 704–710.

[20] X. Ding, W. Ho, J. Shang, L. Zhang, Self doping promoted photocatalytic removal of no under visible light with bi2moo6: Indispensable role of superoxide ions, Appl. Catal. B: Environ., 182 (2016) 316–325.

[21] Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R.L. Davis, K. Jørgensen, W.-J. Xiao, Highly Efficient Aerobic Oxidative Hydroxylation of Arylboronic Acids: Photoredox Catalysis Using Visible Light, Angew. Chem. Int. Ed. 51 (2012) 784–788.

[22] P. Zhang, T. Wang, X. Chang, J. Gong, Effective Charge Carrier Utilization in Photocatalytic Conversions, Acc. Chem. Res. 49 (2016) 911–921.

[23] Z.-A. Lan, W. Ren, X. Chen, Y. Zhang, X. Wang, Conjugated donor-acceptor polymer photocatalysts with electron-output "tentacles" for efficient hydrogen evolution, Appl. Catal. B: Environ. 245 (2019) 596-603.

[24] S. Zang, G. Zhang, Z.-A. Lan, D. Zheng, X. Wang, Enhancement of Photocatalytic H<sub>2</sub> Evolution on Pyrene-based Polymer Promoted by MoS<sub>2</sub> and Visible Light, Appl. Catal. B: Environ. 251 (2019) 102-111.

[25] Z.-A. Lan, G. Zhang, X. Chen, Y. Zhang, K.A.I. Zhang, X. Wang, Reducing the Exciton Binding Energy of Donor-Acceptor-Based Conjugated Polymers to Promote Charge-Induced Reactions, Angew. Chem. Int. Ed. 58 (2019) 10236 –10240.

[26] D. Liu, J. Wang, X. Bai, R. Zong, Y. Zhu, Self-Assembled PDINH Supramolecular System for Photocatalysis under Visible Light, Adv. Mater. 28 (2016) 7284–7290.

[27] P. Zhang, T. Wang, X. Chang, J. Gong, Effective charge carrier utilization in photocatalytic conversions, Acc. Chem. Res. 49 (2016) 911–921.

[28] M.J. Bojdys, J.-O. Müller, M. Antonietti, A. Thomas, Ionothermal Synthesis of Crystalline, Condensed, Graphitic Carbon Nitride, Chem. Eur. J. 14 (2008) 8177.

[29] H. Ou, L. Lin, Y. Zheng, P. Yang, Y. Fang, X. Wang, Tri-s-triazine-Based Crystalline Carbon Nitride Nanosheets for an Improved Hydrogen Evolution, Adv. Mater. (2017) 1700008.

[30] Y. Wang, W. Yang, X. Chen, J. Wang, Y. Zhu, Photocatalytic activity enhancement of coreshell structure  $g-C_3N_4$  (*a*TiO<sub>2</sub> via controlled ultrathin  $g-C_3N_4$  layer, Appl. Catal. B: Environ. 220 (2018) 337-347.

[31] L. Lin, Z. Yu, X. Wang, Crystalline Carbon Nitride Semiconductors for Photocatalytic Water Splitting, Angew. Chem. Int. Ed. 58 (2019) 6164-6175.

[32] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A Metal-free polymeric Photocatalyst for Hydrogen Production from Water under Visible Light, Nature Materials, 8 (2009) 76-82.

[33] W.-J. Ong, L.-L. Tan, Y.H, Ng, S.-T. Yong, S.-P. Chai, Graphitic Carbon Nitride (g-C<sub>3</sub>N<sub>4</sub>)Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a
Step Closer To Achieving Sustainability? Chem. Rev. 116 (2016) 7159-7329.

[34] W. Wang, T. An, G. Li, D. Xia, H. Zhao, J.C. Yu, P.K. Wong, Earth-abundant  $Ni_2P/g-C_3N_4$ lamellar nanohydrids for enhanced photocatalytic hydrogen evolution and bacterial inactivation under visible light irradiation, Appl. Catal. B: Environ. 217 (2017) 570-580.

[35] Y. Ham, K. Maeda, D. Cha, K. Takanabe, K. Domen, Synthesis and Photocatalytic Activity of Poly (triazine imide). Chem. Asian J. 8 (2013) 218.

[36] Y. Chen, B. Wang, S. Lin, Y. Zhang, X. Wang, Activation of  $n \rightarrow \pi^*$  Transitions in Two-Dimensional Conjugated Polymers for Visible Light Photocatalysis, J. Phys. Chem. C. 118 (2014) 29981–29989.

[37] H. Wang, X. Sun, D. Li, X. Zhang, S. Chen, W. Shao, Y. Tian, Y. Xie, Boosting Hot-Electron Generation: Exciton Dissociation at the Order–Disorder Interfaces in Polymeric Photocatalysts, J. Am. Chem. Soc. 139 (2017) 2468–2473.

[38] M.K. Bhunia, K. Yamauchi, K. Takanabe, Harvesting Solar Light with Crystalline Carbon Nitrides for Efficient Photocatalytic Hydrogen Evolution, Angew. Chem. Int. Ed. 53 (2014) 11001–11005.

[39] K. Schwinghammer, M.B. Mesch, V. Duppel, C. Ziegler, J. Senker, B.V. Lotsch, Crystalline Carbon Nitride Nanosheets for Improved Visible-Light Hydrogen Evolution, J. Am. Chem. Soc. 136 (2014) 1730–1733. [40] L. Lin, C. Wang, W. Ren, H. Ou, Y. Zhang, X. Wang, Photocatalytic Overall Water Splitting by Conjugated Semiconductors with Crystalline Poly (triazine imide) Frameworks, Chem. Sci. 8 (2017) 5506-5511.

[41] Z.-A. Lan, G. Zhang, X. Wang, A facile synthesis of Br-modified g-C<sub>3</sub>N<sub>4</sub> semiconductors for photoredox water splitting, Appl. Catal. B: Environ. 192 (2016) 116-125.

[42] G. Zhang, G. Li, Z.-A; Lan, L. Lin, A. Savateev, T. Heil, S. Zafeiratos, X. Wang, M. Antonietti, Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity, Angew. Chem. 129 (2017) 13630–13634.

[43] Y. Noda, C. Merschjann, J. Tarábek, P. Amsalem, N. Koch, M.J. Bojdys, Directional Charge Transport in Layered Two-Dimensional Triazine Based Graphitic Carbon Nitride. Angew. Chem. Int. Ed. 58 (2019) 9394 –9398.

[44] A. Savateev1, S. Pronkin, M. Willinger, M. Antonietti1, and D. Dontsova, Towards organic zeolites and inclusion catalysts: heptazine imide salts can exchange metal cations in the solid state, Chem. Asian J. 12 (2017) 1517-1522.

[45] W. Wu, J. Zhang, W. Fan, Z. Li, L. Wang, X. Li, Y. Wang, R. Wang, J. Zheng, M. Wu, H. Zeng, Remedying Defects in Carbon Nitride to Improve both Photooxidation and H<sub>2</sub> Generation Efficiencies, ACS Catal. 6 (2016) 3365.

[46] L. Lin, H. Ou, Y. Zhang, X. Wang, Tri-s-triazine-Based Crystalline Graphitic Carbon Nitrides for Highly Efficient Hydrogen Evolution Photocatalysis, ACS Catal. 6 (2016) 3921–3931. [47] X. Sun, X. Luo, X. Zhang, J. Xie, S. Jin, H. Wang, X. Zheng, X. Wu, Y. Xie, Enhanced Superoxide Generation on Defective Surfaces for Selective Photooxidation, J. Am. Chem. Soc. 141 (2019) 3797–3801.

[48] F. Amano, K. Nogami, B. Ohtani, Enhanced photocatalytic activity of bismuth-tungsten mixed oxides for oxidative decomposition of acetaldehyde under visible light irradiation. Catalysis Communications 20 (2012) 12–16.

[49] R.E. Maleczka, F. Shi, D. Holmes, M. R. Smith, C–H Activation/ Borylation/ Oxidation: A One-Pot Unified Route to Meta-Substituted Phenols Bearing Ortho-/ Para-Directing Groups, J. Am. Chem. Soc. 125 (2003) 7792-7793.

[50] J. Xu, X. Wang, C. Shao, D. Su, G. Cheng, Y. Hu, Highly Efficient Synthesis of Phenols by Copper-Catalyzed Oxidative Hydroxylation of Arylboronic Acids at Room Temperature in Water, Org. Lett. 12, (2010) 1964-1967.

[51] K. Inamoto, K. Nozawa, M. Yonemoto, Y. Kondo, Micellar system in copper-catalysed hydroxylation of arylboronic acids: facile access to phenols, Chem. Commun. 47 (2011) 11775–11777.

[52] A.-S. Ding, Y. Zhang, Y. Chen, R. Rios, J. Hu, H. Guo, Visible light induced oxidative hydroxylation of boronic acids, Tetrahedron Letters 60 (2019) 660–663.

[53] J. Luo, X. Zhang, J. Zhang, Carbazolic Porous Organic Framework as an Efficient, Metal-Free Visible-Light Photocatalyst for Organic Synthesis. ACS Catal. 5 (2015) 2250-2254.

[54] S.P. Pitre, C.D. McTiernan, H. Ismaili, J.C. Scaiano, Mechanistic Insights and Kinetic Analysis for the Oxidative Hydroxylation of Arylboronic Acids by Visible Light Photoredox Catalysis: A Metal-Free Alternative, J. Am. Chem. Soc. 135 (2013) 13286-13289.

[55] Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu, X. Wang, Metal-free activation of  $H_2O_2$  by g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation for the degradation of organic pollutants, Phys. Chem. Chem. Phys., 14 (2012) 1455–1462.

[56] P.-F. Wei, M.-Z. Qi, Z.-P. Wang, S.-Y. Ding, W. Yu, Q. Liu, L.-K. Wang, H.-Z. Wang, W.-K. An, W. Wang, Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis, J. Am. Chem. Soc. 140 (2018) 4623–4631.

## Graphical Abstracts



We optimized the crystallization process of carbon nitride polymer by selecting precursors of different polymerization degrees with a molten salt method. Benefiting from the high crystallinity, extended  $\pi$ -conjugated system and strong van der-Waals interactions between interlayers, the modified carbon nitride polymer exhibited accelerated charge transport and enhancement in electron induced molecular oxygen activation reactions under visible light, such as hydroxylation of phenylboronic acid and degradation of organic pollutant RhB.

# Highlights

(1) The crystallization process of carbon nitride polymer photocatalysts has been optimized for

promoting the molecular oxygen activation performance.

- (2) Subsequent experiments prove that more extended  $\pi$ -conjugated system and tighter layer-tolayer stacks can significantly boost the photogenic carrier migration and superior photocatalytic performance of CCN.
- (3) The optimal CCN lead to the excellent conversion of phenylboric acid with over 99% selectivity, as well as 6-fold higher activity in Rh B photodegradation.
- (4) The mechanism studies of these two representative reactions have been further investigated to understand the advantages of CCN in catalyzing ROS-induced reactions.