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A composite polymeric carbon nitride with *in situ* formed isotype heterojunctions for highly improved photocatalysis under visible light

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Abstract: Introducing heterojunction is an effective way for improving the intrinsic photocatalytic activity of a graphitic carbon nitride (GCN) semiconductor. These heterostructures are mostly introduced by interfacing GCN with foreign materials that normally have entirely different physicochemical properties and shows unfavorable compatibility, thus resulting in a limited improvement of the photocatalytic performance of the resultant materials. Herein, a composite polymeric carbon nitride (CPCN) that contains both melon-based GCN and triazine-based crystalline carbon nitride (CCN) was prepared by a simple thermal reaction between lithium chloride and GCN. Thanks to the intimate contact and good compatibility between GCN and CCN, an *in situ* formed heterojunction acts as a driving force for separating the photogenerated charge carriers in CPCN. As a result, CPCN exhibits a significantly improved photocatalytic performance under visible light irradiation, which is respectively 10.6 and 5.3 times as high as those of the GCN and CCN alone. This well designed isotype heterojunction by a coupling of CCN presents an effective avenue for developing efficient GCN photocatalysts.

1. Introduction

Semiconductor-based photocatalysis has been considering as one of the most promising technologies to solve energy and environmental issues in the effective ways of solar energy conversion and water purification.¹ Generally, there are three main processes involved in the photocatalytic process: (1) the production of charge carriers (holes and electrons) with light excitation; (2) the separation and transfer of charge carriers in space to prevent their recombination; (3) the redox reactions at the surface of semiconductors.² In particular, among these steps, the separation efficiency of the photoexcited charge carriers plays the most crucial role in the final efficiency of a given semiconductor photocatalyst.³ In most cases, due to the strong function of the built-in electric field of heterostructures, the construction of heterojunctions through interfacing of different semiconductors is deemed as one of the most effective strategies for reducing the recombination probability of photoexcited charge carriers and thus greatly improving the photocatalytic performance.^{3b, 4}

In recently years, organic conjugated polymers, characterized by delocalized π -conjugated electrons, such as graphitic carbon nitride (GCN),⁵ planarized conjugated polymer (PCP),⁶ conjugated triazine frameworks (CTF),⁷ covalent organic frameworks (CMF),⁸ and conjugated microporous polymers (CMP)⁹ have been receiving increasing interest as a new family of promising photocatalysts for solar energy conversion.¹⁰ In particular, due to the unique layered structure, easy availability, outstanding chemical and thermal stability, and appealing molecular structure with adequate band edges, GCN-based photocatalysts have been widely regarded as one of the most fascinating metal-free solar light-driven photocatalysts since the pioneering study by Wang *et al.* in 2009.^{3b, 11} Nevertheless, the traditional GCN based on melon structure exhibits inherently limited photocatalytic activity due to the rapid recombination of photogenerated charge carriers caused by the low crystallinity and intrinsic π -conjugated heterocyclic structure (tri-s-triazine).^{1b, 7} There have been extensive studies in improving

the photocatalytic performance of GCN by various ways, such as designing novel nanostructures,¹² tuning chemical composition,^{7, 13} doping with heteroatoms,¹⁴ constructing heterojunctions.¹⁵ Among these, introducing heterostructures in GCNs is the most often used since the tunable band structure enables GCN to be an excellent candidate for coupling with carbon nanomaterials,¹⁶ noble metal nanoparticles,¹⁷ and various semiconductor materials, such as TiO₂,¹⁸ ZnO,¹⁹ Ag₃PO₄,²⁰ AgX,²¹ Ag₂O,²² MoS₂,²³ DyVO₄,²⁴ and Fe₂O₃.²⁵ Most of the heterostructures reported thus far were developed by introducing external semiconductors. However, the extraneous materials usually show remarkably different physicochemical properties from GCN, which may greatly influence the compatibility, homogeneity, and stability of the resultant heterojunctions, and also weaken the inherent advantages of GCN. Therefore, constructing an isotype heterojunction by interfacing two different crystal phases of a same semiconducting material is an alternative and better approach.²⁶ Zhang *et al.* first reported an isotype heterojunction in GCN through coupling two types of GCNs with different band gap structures prepared from different precursors.^{15b} Following this, several groups have also prepared isotype heterojunctions through interfacing differently structured GCNs.^{26b, 27} Despite these advances, it is urgently desired to improve the crystallinity and band offset of the isotype heterojunction to further improve the photocatalytic performance.

Recently, another n-type polymeric carbon nitride semiconductor, known as crystalline carbon nitride (CCN), which is composed of imide linked triazine motif, has received much attention in photocatalysis due to its high crystallinity, good condensed conjugation structure, and narrow band gap.^{7, 28} Previous studies have shown that in some cases, CCN even show higher visible-light driven photocatalytic activity than GCNs due to the wider absorption of light and better photoresponse.^{28c, 29} However, the photocatalytic performance of CCN is also limited by the fast recombination of photoexcited charge carriers owing to the extended π -electron system. Considering the obviously

different band structures of GCN and CCN, a combination to form an isotype heterojunction may be a novel and effective approach to address the drawbacks mentioned earlier.

Motivated by the above discussion, we here proposed and prepared a composite polymeric carbon nitride (CPCN) that contains GCN and CCN through a simple thermal reaction of GCN and LiCl, where an isotype heterojunction is naturally formed at the interface between GCN and CCN. The different electronic band structures in GCN and CCN ensures a good matching between CB and VB levels. As expected, the resultant CPCN photocatalyst exhibits highly improved activity for the photocatalytic degradation of RhB over GCN and CCN under visible light irradiation. Such a strategy by interfacing and coupling GCN with CCN to form an isotype heterojunction is believed to be an effective route for developing efficient GCN photocatalysts for sustainable energy.

2. Results and Discussion

The detailed process for CPCN preparation is represented in **Scheme 1**. Such a strategy helps construct an interface between CCN and GCN, facilitating the transfer of photogenerated charge carriers due to their synergistic effect. It is noted that LiCl plays a critical role in the formation of CCN through the thermal reaction with GCN. This was demonstrated by the comparison of thermogravimetric analysis (TGA)/ differential scanning calorimetry (DSC) results with those of pristine GCN and LiCl (Figure S1). As such, the formation of CPCN was obviously influenced by the weight ratio of LiCl to GCN. The resultant sample labeled as CPCN- x , where $x = (0.3, 0.6, 1, \text{ and } 2)$, refers to the mass of LiCl relative to GCN as 0.3, 0.6, 1.0, and 2.0, respectively. Since the CPCN-0.6 showed the highest photocatalytic activity (see detail discussion below), the CPCN presented in this work defaults to the CPCN-0.6 unless otherwise specified.

The crystalline structure of CPCN was analyzed by XRD in comparison with that of GCN and CCN. Similar to previously reported results, two peaks located at 13.2° and 27.4° that are respectively ascribed to the in-plane repeating unit and the stacking of the conjugated aromatic system are found in the XRD pattern of GCN (**Figure 1A**).^{11a} For the XRD pattern of CCN, all the diffraction peaks are consistent with those of the poly (triazine imide) incorporated with Li^+ and Cl^- ions (CCDC No. 902173).³⁰ The XRD pattern of CPCN contains the characteristic peaks of both GCN and CCN, suggesting the coexistence of the GCN and CCN in CPCN. A more careful observation reveals that the typical peaks of GCN and CCN in the XRD pattern of CPCN show a remarkable intensity decrease and the (002) peak of GCN almost disappears compared to that of GCN, suggesting the possible delamination of the GCN due to the incorporation of CCN. The chemical structure of CPCN is confirmed by FTIR measurement. As shown in Figure 1B, the GCN, CPCN, and CCN show the typical FTIR spectra of carbon nitride that have one sharp peak at 808 cm^{-1} , several peaks ranging from 1200 to 1600 cm^{-1} , and one broad peak between 3000 and 3550 cm^{-1} .^{1a, 12c} These characteristic bands are respectively ascribed to the unique breathing modes of triazine ring, the stretching vibrations of CN heterocycles, and stretching modes of N-H and H-O bonds. In addition, the FTIR spectra of both GCN and CPCN show one stronger peak at about 2200 cm^{-1} that corresponds to the stretching vibration of the terminal cyano group ($\text{C}\equiv\text{N}$) compared to that of the GCN,^{29b, 31} indicating the presence of CCN. A weak peak at about 1080 cm^{-1} associated the stretching mode of C-O bonds was found in the FTIR spectra of CPCN, suggesting the existence of functional oxygen in the CPCN.³²

The chemical compositions of CPCN were studied by XPS technique. The survey XPS spectra shown in Figure 1C reveal the presence of C (288.5 eV), N (389.9 eV), and O (532.6 eV) elements in both GCN and CPCN.^{7, 12a, 12c} Quantitative analysis reveals a close N/C molar ratio of 1.30 for GCN

and 1.27 for GPCN (Table S1), suggesting the retention of aromatic C/N heterocyclic structure in CPCN. However, the XPS spectrum of CPCN reveals the emergence of a weak peak of the Li 1s at a low-binding energy of 55.5 eV, as well as a weak peak of Cl 2p at 199.6 eV that indicate the presence of CCN in CPCN.³¹ This is further confirmed by the high-resolution XPS spectra of Li 1s and Cl 2p (Figure S2). Furthermore, the O 1s peak of CPCN is much stronger than that of GCN, suggesting the higher content of oxygen of CPCN due to the higher specific surface area and the possible presence of doping oxygen. The high resolution O 1s spectrum of GCN can be fitted to one peak at 532.9, corresponding to the adsorbed oxygen on the surface. Another peak at 531.6 eV ascribed to the C-O appears in the O 1s spectrum of CPCN (Figure 1F),^{32a} suggesting that CPCN was functionalized with oxygen after the intercalation of LiCl. This is also confirmed by the C 1s spectrum. The functionalized oxygen may result from the oxidization of the highly reactive intermediates from the decomposition of GCN during the washing process. Note that the high content of oxygen in the CPCN is very helpful for photocatalysis due to the better dispersibility in water. As shown in Figure 1D, the C 1s peaks of CPCN can be resolved into four peaks at 289.7 eV (C-O), 288.0 (N-C), 286.5 (N=C or N≡C), and 284.9 eV (sp² C=C). However, there are two peaks at 288.4 and 285.2 eV in the C 1s peaks of GCN.^{12b, 12i} Furthermore, the binding energy of C 1s of CPCN is slightly shifted towards higher energies compared to that of the pristine GCN, indicating that there is a charge transfer between GCN and CCN due to their interaction. Moreover, both the N 1s spectrum of GCN and CPCN can be fitted into four peaks at 403.9, 401.0, 399.2, and 398.6 eV (Figure 1E), corresponding to the positive charge localization (π -excitations), amino or imino functions (H-N-C), tertiary nitrogen (C)₃-N, and the sp²-hybridized nitrogen (C-N=C) or cyano groups (N≡C) in the basic triazine heterocyclic ring units of the polymeric carbon nitrides, respectively.^{12a, 12c, 14a, 31, 33} All these results confirmed that the CPCN is composed of GCN and CCN.

Coupling GCN with CCN should have significant effect on the optical and structural properties of the GCN. In this case, the UV-vis diffuse reflectance spectroscopy (DRS) was used to study the optical absorption that plays an important role in the photocatalytic performance. The DRS spectra in **Figure 2A** clearly show that the absorption edge of CPCN reveals an obvious red shift from 465 to 780 nm compared to that of GCN. The red shift of the optical absorption is also reflected in the color change from yellow of GCN to red of CPCN (inset in **Figure 2A**) and the much smaller bandgap energy (**Figure S3**). The apparent improvement in the absorption intensity in the full spectrum range and a remarkable red shift of the absorption edge may be attributed to the isotype heterojunction and the presence of functional oxygen groups,^{27b-d, 32a} and is highly favorable for photocatalytic reaction. In order to study the structural change of GCN after in-situ introduction of CCN, the porosity and specific surface area (SSA) were determined by the N₂ adsorption-desorption isotherms in detail. As shown in **Figure 2B**, CPCN show a typical IV type isotherm with an obvious hysteresis loop in the relative pressure (P/P_0) of 0.6-0.9 region while the pristine GCN shows an isotherm without any hysteresis loop. The SSA calculated by Brunauer-Emmett-Teller (BET) method of CPCN and GCN are 31 and 6 m² g⁻¹, respectively. The higher SSA of CPCN may be attributed to the pores produced by the decomposing process of GCN and the reaction between LiCl and GCN. The pore size distribution curve (PSD) obtained by Barrett-Joyner-Halenda (BJH) method clearly reveals the presence of a mesoporous structure of CPCN with the size ranging from 2 to 50 nm, while the PSD curve of GCN shows no peak. The mesoporous structure and higher SSA of CPCN are also conducive to the photocatalytic reaction due to more active sites.

The porous structure and lamellar morphology of the samples were further observed by electron microscope. The scanning electron microscope (SEM) images shown in **Figures 3A** and **3B**, the pristine GCN shows irregularly shaped particles while CPCN is composed of lamellar particles and

smaller grain with rough surface. The magnified SEM image further shows that the lamellar structure of CPCN are wrinkled and porous (Figures 3C and S2). Some small pores are inside the lamellar particles and some big pores are in-plane holes. The average thickness of the lamellar structure is about 50 nm. A further increase in magnification of the SEM image reveals that there are many spherical nanoparticles with the average size of about 20 nm attached closely on the surface of the lamellar structure in CPCN (Figure 3D). The microstructure of CPCN is further examined by transmission electron microscope (TEM). As shown in **Figure 4A**, the CPCN are composed of a porous tabular structure loaded with many darker contrast spherical nanoparticles, which is in good agreement with the SEM observation. At higher magnification (Figure 4B), many scratch-like structures with many in-plane holes can be clearly seen (Figure S3). The scratch-like and mesoporous features of CPCN may be caused by the etching of LiCl through the chemical reaction with GCN. Furthermore, the selected area electron diffraction (SAED) pattern reveals a series characteristic diffraction rings of CCN (inset in Figure 4A), suggesting the polycrystalline structure of CCN in CPCN. This is consistent with the XRD results. A high-resolution TEM (HRTEM) image of CPCN further reveals the crystalline feature of the CCN (Figure 4C). The denoted lattice fringes showing the interlayer spacing of 0.31 and 0.38 nm are respectively ascribed to the (012) and (020) crystal planes of CCN. It can be also seen that the CCN were uniform distributed and anchored in the amorphous GCN matrix. Such an intimate contact between GCN and CCN results in the isotype heterojunction in the CPCN. Furthermore, the analogous layered structures, similar compositions, and the specific properties of the van der Waals force are also very helpful for the heterojunction formation between GCN and CCN.

We evaluated the photocatalytic performance of various CPCN samples toward the degradation of RhB aqueous solution under visible light irradiation in comparison to pristine GCN and CCN (see the

experimental section for details). As shown in **Figure 5A**, the blank test indicates that almost negligible RhB was degraded under visible light without any catalyst. The GCN, CPCN-0.3, CPCN-0.6, CPCN-1.0, CPCN-2.0, and CCN can respectively achieve a photocatalytic RhB degradation efficiency of 23.1%, 49.0%, 93.3%, 78.9%, 53.0%, and 44.0% after 2.5 h under visible light irradiation. From the linear fitting of illumination time versus $-\ln(C/C_0)$ using the pseudo-first-order kinetics model (Figure S5), we obtain the ideal rate constant of 0.10, 0.23, 1.06, 0.60, 0.27 and 0.20 h^{-1} for GCN, CPCN-0.3, CPCN-0.6, CPCN-1.0, CPCN-2.0, and CCN, respectively (Figure 5B). It can be clearly seen that the all the CPCN samples exhibit higher photocatalytic activity than that of pristine GCN and pure CCN. The photodegradation activity of CPCN-0.6 for RhB is about 10.6 and 5.3 times higher than that of pure GCN and CCN. The photocatalytic performance of CPCN is also better than that of many reported GCN-based composite photocatalysts (Table S2). Note that the simple mixture of GCN and CCN show no obviously improved photocatalytic performance, suggesting the interface interaction induced heterojunction formation is required for the photocatalytic reaction. Besides, six cyclic photocatalytic experiments indicate that CPCN also has a good reusability for RhB degradation under visible light irradiation (Figure S6). The retentive morphology and structure suggests the acceptable stability of CPCN during the photocatalytic reaction (Figure S7). The slight decay of photocatalytic activity is possibly due to the unavoidable loss of CPCN during the recovery process. Further studies is still needed to improve the activity and stability for more applications like water splitting and carbon dioxide reduction.

To identify the possible reactive radicals of the CPCN accounting for RhB degradation, photocatalytic measurements with various trapping agents were performed in detail. According to previous reports, the 1,4-benzoquinone, ethylenediamine teraacetic acid disodium (EDTA-2Na), and tertiary butanol (*t*-BuOH) were respectively used as the scavengers for superoxide radical ($\cdot\text{O}_2^-$),

photoexcited holes (h^+), and hydroxyl radicals ($\cdot OH$).³⁴ It is found that the photocatalytic degradation of RhB is obviously suppressed after the addition of 1, 4-benzoquinone (Figure S8). The photocatalytic RhB degradation efficiency decreased from 93.3% without any scavengers to 13.4% as most $\cdot O_2^-$ is removed by 1,4-benzoquinone. This is also supported by the argon purging experiment that shows the degradation efficiency of RhB decrease to 31.6%. In addition, after the holes were trapped by EDTA-2Na, the degradation efficiency also became lower with a value of 46.6%. After introducing *t*-BuOH during the photocatalytic experiment, CPCN exhibits a negligible inhibition with a high degradation efficiency of 86.6%, indicating that $\cdot OH$ species are not the dominated reactive species. The trapping experiment results confirm that the $\cdot O_2^-$ and h^+ rather than the $\cdot OH$ are the active species for the RhB degradation in the photocatalytic system over CPCN under visible light irradiation. This is associated with the band structures of GCN and CCN.

To reveal the mechanism of highly improved photocatalytic activity of the CPCN, the photoluminescent and photochemical properties of CPCN were carefully studied in comparison to those of GCN. The separation and recombination behavior of the photogenerated charge carriers were first studied by PL spectra obtained with an excitation wavelength of 400 nm at room-temperature. As shown in **Figure 6A**, GCN exhibits a strong and broad emission peak centered at about 460 nm corresponding to the intrinsic PL emission of GCN due to the recombination of photoexcited charge carriers. In contrast, the CPCN shows ignorable emission intensity in the same condition, suggesting an obvious suppressed recombination of the photoexcited electron-hole pairs in the CPCN. This is also confirmed by the photoelectrochemical results reflected by electrochemical impedance spectroscopy (EIS) and photocurrent measurements. As shown in **Figure 6B**, the semicircular Nyquist plots of the CPCN-based electrode show obviously reduced diameter than those of the GCN both in darkens and under visible light irradiation, suggesting the significantly improved charge transfer in

the CPCN. This is further confirmed by the greatly increased photocurrent generated on the electrode based on CPCN (inset in Figure 6B). These results imply that the synergetic interaction between CCN and GCN significantly facilitates charge mobility and separation by forming a phase-like heterojunction. Interestingly, the coupling of CCN also obviously changes the electron paramagnetic resonance (EPR) spectra of the GCN at room temperature. As shown in Figure 6C, both GCN and CPCN show one paramagnetic line with the g value of 2.0035 ascribed to lone pair electrons on the sp^2 -carbon atoms of the aromatic heterocyclic rings in the π -conjugated system.^{15b} However, the EPR signal of the CPCN shows a much increase in the intensity compared to that of the GCN. A much increased EPR signal can be observed in the CPCN under visible light irradiation in comparison to GCN, implying a more efficient photoexcited production of radical species in the CPCN (Figure 6D). In addition, the CPCN still exhibits a much stronger EPR signal while the GCN shows the negligible EPR signal after subtracting the background after the light off. This is presumably due to the improved delocalization of π -electrons in the conjugated system of the CPCN caused by the heterojunction formed between CCN and GCN. Furthermore, the functionalization with oxygen would offer extra electrons in the CPCN in analogy to O-doped GCN system because an oxygen atom has one more electron than a nitrogen atom. The extra electrons can be redistributed to the nearest carbon atoms, resulting in the delocalization of π electrons in the conjugated heterocyclic ring of the GCN and CCN.^{32a} Besides, although the BET SSA of the CPCN is about five times higher than that of GCN, the internal activity of the CPCN based on normalization of activity to SSA still outperforms that of GCN, suggesting the important role of isotype heterojunction between GCN and CCN in promoting the photocatalytic reaction.

To identify the possible band gap structure of the CPCN, Mott-Schottky (MS) analysis was carried out in detail. The MS plots of both ideal GCN and CCN exhibit a positive slope (Figure S9), implying

their intrinsic n-type conductivities. By extracting the linear part of the MS curves, the flat-band potential that is close to the CB position of CCN and GCN were estimated to be -0.90 and -1.10 V versus *NHE* at various frequencies. Although the actual band gap structures of CCN and GCN in CPCN may be different from the above assumption, the different flat band potential indicates that a build-in electric field can be formed on the heterojunction interface between GCN and CCN. Based on the above analysis, a possible mechanism was proposed to explain the better separation and transportation of charge carriers in the CPCN (Figure S10). Upon visible light irradiation, both CCN and GCN can be excited to produce electrons and holes. In the isotype heterostructures based CPCN photocatalyst, the photoexcited electrons in the CB of GCN tend to transfer rapidly to the CB of the CCN due to inner electric field caused by the difference edge potential and the band levels of GCN and CCN. Due to the more positive redox potential of $O_2/\cdot O_2^-$ (-0.046 V) than the CB edge potential of GCN (-0.90 eV) and CCN (-1.10 V), the separated electrons on the surface of CPCN can reduce the dissolved O_2 in the aqueous solution into highly active $\cdot O_2^-$. In addition, there are abundant holes remained in the VBs of GCN and CCN. These remained holes may be also transferred between CCN and GCN due to the reaction kinetics and inner electric fields (Figure S10). However, the VB potential of GCN (1.56 eV) and CCN (1.56 eV) is more negative compared with the standard reduction potential of $\cdot OH/OH^-$ (1.99 eV). As a result, most of the photoexcited holes accumulated on the surface of CPCN cannot oxidize the OH^- into $\cdot OH$ species. Even so, these active holes are able to directly decompose the RhB molecular and will be consumed in the photocatalytic degradation process. It can be seen that the $\cdot O_2^-$ and h^+ active radicals are the main reactive species, in agreement with the above trapping experimental results and previous reports.³⁴ Note that this photoreaction mechanism in the CPCN is based on the ideal band gap structures of CCN and GCN. It needs to be further elucidated in detail in the future since the band structures of CCN and GCN are highly related to the degree of crystallinity and the compositions.³⁵ This is also confirmed by the result that the

CPCN prepared with different of LiCl showed different photocatalytic performance. As a whole, the isotype heterojunction between GCN and CCN greatly improve the separation efficiencies of photogenerated electron-hole pairs and significantly decreases the probability of electron-hole recombination, which is of great importance for improving photocatalytic activity of CPCN. Some experiments by using the as-synthesized CPCN for water splitting and carbon dioxide reduction is under way by optimizing the reaction condition.

3. Conclusion

A composite polymeric carbon nitride (CPCN) photocatalyst with an *in situ* formed isotype heterostructure of GCN/CCN has been prepared through a simple thermal reaction of LiCl with GCN, where CCN is produced and interfaced with GCN. This approach is simple and easily scalable. The resultant CPCN shows much higher photocatalytic performance and stability than mono-component GCN and CCN towards the degradation of RhB under visible light irradiation. The highly improved photocatalysis of CPCN is resulted from the isotype heterojunction-induced high efficiency separation and transfer of the photoexcited electrons and holes. The as-prepared CPCN may be also a good photocatalyst for other solar energy utilization, such as water splitting, CO₂ redcuton, and so on. As a whole, the formation of an isotype heterojunctions through CCN coupling presents a new and ideal avenue to develop efficient GCN-based photocatalysts, which is of great importance for energy and photoelectronic devices.

4. Experimental Section

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1 The proposed approach for the preparation of CPCN.

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Figure 1 XRD patterns (A), FTIR (B), XPS survey spectra (C), high resolution C1s (B), N1s (C), and O1s (D) XPS spectra of GCN (a) and CPCN (b).

Figure 2 DRS (A) and N₂ isotherm lines (B) of GCN (a) and CPCN (b). The insets in (B) are the corresponding pore size distribution curves.

Figure 3 SEM images of GCN (A) and CPCN (B-D). The arrows in (B) and (D) indicate the pores structure of the CPCN flakes.

Figure 4 TEM (A and B) and HRTEM images and the corresponding line profiles (C) of CPCN. The inset in (A) is the corresponding SAED pattern.

Figure 5 Photocatalytic degradation curves (A) and the reaction rate constants obtained by a kinetic linear simulation (B) of RhB degraded by different samples under visible light irradiation.

Figure 6 PL spectra (A), EIS spectra and photocurrent curves (B), and the EPR spectra measured in darkness (C), and with lights on (D) and after light off (E) of GCN (a) and CPCN (b).

The table of contents: A heterostructural composite polymeric carbon nitride that contains both melon-based graphitic carbon nitride and triazine-based crystalline carbon nitride exhibits a significantly improved photocatalytic performance under visible light irradiation

Keyword: graphitic carbon nitrides, heterojunction, photocatalysis, charger carriers, visible light

Authors: Qinghua Liang, Zhi Li, Yu Bai, Zheng-Hong Huang,* Feiyu Kang, Quan-Hong Yang*

Title: A composite polymeric carbon nitride with naturally formed isotype heterojunction for highly improved photocatalysis under visible light

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Supporting Information

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A composite polymeric carbon nitride with *in situ* formed isotype heterojunctions for highly improved photocatalysis under visible light

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1. Experimental section

1.1. Preparation of the CPCN

Melamine and lithium chloride of analytical grade were purchased from Beijing Chemical Works and were used as-received without further purification. Deionized water was used throughout our experiments. The composite polymeric carbon nitride was prepared through the *in situ* formation of crystalline carbon nitride (CCN) based on the reaction between graphitic carbon nitride (GCN) and LiCl. The reason for choosing LiCl as the reactant is that LiCl was widely used as reactant and molten salt for preparing CCN (Chem. Eur. J. 2011, 17, 3213; Chem. Asian J. 2013, 8, 218; ACS Catalysis, 2016, 3921). Typically, GCN was first prepared by a thermal polymerization of melamine. Subsequently, 1.0 g of the resultant GCN was uniformly mixed with a certain amount of lithium chloride. Then, the mixture was subjected to a further thermal treatment at 600 °C under inert atmosphere for 2 h. The as-obtained samples were washed thoroughly with deionized water to remove the soluble substance. Finally, CPCN was obtained after drying at 80 °C for overnight. The resultant sample was labeled as CPCN-x, where x = (0.3, 0.6, 1, and 2) refers to the mass of LiCl as 0.3, 0.6, 1.0, and 2.0 g, respectively. In particular, CPCN-0.6 was chosen for the current study since our preliminary photocatalytic studies suggest that the CPCN prepared when the mass ratio of LiCl and GCN is 0.6 showed the best performance (see discussion below for details). Note that the physical mixture of CCN and GCN failed to produce close interconnection between CCN and GCN. The referenced CCN was prepared according to our previous report (Q. Liang, Z.-H. Huang, F. Kang, Q.-H. Yang, ChemCatChem, 2015, 2897-2902).

1.2 Materials characterization

The powder X-ray diffraction (XRD) patterns were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation with an accelerating voltage of 40 kV. The morphology and structures were carefully observed by field emission scanning electron microscope (SEM, Hitachi S-4300) and transmission electron microscope (TEM, JEOL JEM-2100F). The accelerating voltages of the SEM and TEM observation are 10 and 200 kV, respectively. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was carried out to determine the surface chemical composition. During the XPS measurements, a non-monochromatized Al-K α (1486.7 eV) was used as the X-ray excitation source,

and the C 1s peak at 284.8 eV was adopted as an internal standard to correct the binding energies. The diffuse reflection spectra (DRS) were collected on a UV-Vis-NIR spectrophotometer (Varian, Cary 5000) using BaSO₄ pellets as the reference reflectance. Fourier transformed infrared (FTIR) spectra were carried out on a VERTEX-70 FTIR spectrometer using KBr powder as the matrix. The powder photoluminescence (PL) spectra were measured on a fluorescence photometer (Varian, Cary Eclipse) with a spherical integrating sphere. The nitrogen adsorption at 77 K was tested on a Belsorp mini-II adsorption instrument to determine the specific surface area (SSA) by Brunauer-Emmett-Teller (BET) method. The electron paramagnetic resonance (EPR) spectra were obtained on a Bruker E500 EPR spectrometer. The thermal stability was evaluated on a thermogravimetric analyzer (Mettler-Toledo, TGA/DSC 2) in a N₂ flow of 50 mL min⁻¹. All measurements were performed at room temperature unless particularly specified.

1.3 Electrochemical measurements

The electrochemical measurements performed on a Bio-Logic electrochemical workstation were achieved by a standard three-electrode quartz cell using a working electrode, a Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. A 0.5 M NaSO₄ aqueous solution was used as electrolyte. For fabricating the working electrode, 0.5 mg of the sample was well dispersed in 1.0 mL DMF to produce a stable suspension. Then, this dispersion was well coated on a clean fluorine-tin oxide (FTO) glass with the surface area of 1 cm × 1 cm in a fume hood. After drying at room temperature, the FTO glass was further thermally treated at 260 °C for 2 h under vacuum to obtain the final working electrode. The electrochemical impedance spectroscopy (EIS) was conducted over a frequency range from 200 kHz to 20 mHz with an amplitude of 5 mV. The photocurrent was measured under visible light irradiation with a 300 W Xeon lamp that was placed 15 cm away from the photoelectrochemical cell.

1.4 Photocatalytic experiments

Photocatalytic experiments was carefully evaluated by the degradation of Rhodamine B (RhB) aqueous solution irradiated by a 300 W xenon lamp combined with a 400 nm cut-off filter. The light source was placed about 20 cm vertically away from the photocatalytic reactor. Typically, 30 mg of the powdered catalysts were well dispersed in 200 mL RhB with the concentration of 10 mg L⁻¹.

Then, the suspension was magnetically stirred for 1.5 h in darkness to reach adsorption-desorption equilibrium. Afterwards, the above suspension was irradiated with visible light under magnetic stirring. Then, at a given time intervals, about 2 mL suspension were drawn out with a syringe, filtered with a microspore filter (about 0.2 μm), and analyzed the absorbance at 553 nm by a UV-Vis spectrophotometer (Shimadzu UV-2250). The degradation rate of the above pollutants is represented by C/C_0 , in which C_0 and C refer to the initial and final absorbance of the RhB at 553 nm.

2. Figures and Tables

Figure S1 TGA/DCS curves of GCN, LiCl, and the mixture of GCN and LiCl. The initial temperature is 30 °C. The samples were heated to 600 °C and kept at 600 °C for 2 h under nitrogen atmosphere.

LiCl is very stable and show negligible weight loses even when the temperature was increased to 600 °C. One small peak in the DSC curve of LiCl at about 100 °C is ascribed to the partial loss of crystal water of LiCl. The TGA curve of GCN also shows little weight lose from 30 to 580 °C, ascribing to the removal of the adsorbed water on the surface of GCN. As the temperature increase to above 580 °C, the GCN began to decompose slowly. Note that GCN decomposes more quickly in the presence of LiCl, which may be attributed to the reaction between the molten LiCl and the highly active intermediates produced from the decomposing process of GCN since LiCl has a strong electronic interaction with the electron-rich N-containing species. This reaction is confirmed by the corresponding DSC results. In particular, the DSC curve of the mixture of GCN and LiCl shows a much

higher heat flow at about 580 °C than GCN or LiCl, implying the occurrence of exothermic reaction between LiCl and GCN. It can not be excluded the rearrangement of the GCN from tri-s-triazine to s-triazine that will possibly polymerize with the molten LiCl. Therefore, a comparison of the TGA/DSC results with those of pristine GCN and LiCl led us to conclude that the reaction between LiCl and GCN upon heating process, resulting in the formation of CCN.

Table S1 Chemical composition of GCN and CPCN obtained from XPS.

Sample	C	N	O	Cl	Li
GCN	43.0	55.8	1.2	0	0
CPCN	35.2	44.6	11.6	1.8	6.8

Figure S2 XPS spectra of Cl 2p and Li 1s of CPCN. The Cl 2p XPS spectrum can be resolved two peaks at 198.4 and 200.0 eV. The Li 1s peak can be fitted into one peak at 55.5 eV.

Figure S3 The plots of $(Rh\nu)^{1/2}$ vs photon energy ($h\nu$) for evaluating the band gap energy of CPCN and GCN by Kubelka–Munk method. The band gap of the CPCN (1.70 eV) is much smaller than that of GCN (2.67 eV), suggesting the red shift of light absorption in CPCN.

Figure S4 The SEM (A) and TEM (B) images showing the in-plane holes of CPCN.

Figure S5 The quasi-first-order kinetic curves of the photocatalytic degradation of RhB over different samples under visible light irradiation.

Table S2 Summary of the photocatalytic activities of RhB degradation by various GCN-based composite photocatalysts under visible light.

Heterojunction Material	Preparation Method	Degradation Condition	Light Source	Rate Constant	Normalized Rate ^{&}	Reference
GCN/TiO ₂	Solvothermal	50 mg catalysts	350W Xe lamp $\lambda \geq 420$ nm	2.01 h ⁻¹	0.032 h ⁻¹	[1]
		80 mL, 10 mg L ⁻¹				
GCN/ β -Fe ₂ O ₃	Calcination	200 mg catalysts	300W Xe lamp $\lambda \geq 420$ nm	0.53 h ⁻¹	0.004 h ⁻¹	[2]
		160 mL, 10 mg L ⁻¹				
GCN/ZnS	Template	8.5 mg catalysts	500W Xe lamp $\lambda \geq 400$ nm	2.04 h ⁻¹	0.024 h ⁻¹	[3]
		20 mL, 5 mg L ⁻¹				
GCN/ZnO	Calcination	50 mg catalysts	500W Xe lamp $\lambda \geq 400$ nm	2.20 h ⁻¹	0.005 h ⁻¹	[4]
		25 mL, 4.5 mg L ⁻¹				
GCN/WO ₃	Hydrothermal	50 mg catalysts	500W Xe lamp $\lambda \geq 400$ nm	4.14 h ⁻¹	0.15 h ⁻¹	[5]
		400 mL, 4.8 mg L ⁻¹				

GCN/RGO	Calcination	8 mg catalysts 5 mL, 5 mg L ⁻¹	1000W Xe lamp, $\lambda \geq 400$ nm	3.78 h ⁻¹	0.012 h ⁻¹	[6]
GCN/TiO ₂	Calcination	40 mg catalysts 50 mL, 2.9 mg L ⁻¹	350W Xe lamp $\lambda \geq 420$ nm	2.86 h ⁻¹	0.010 h ⁻¹	[7]
GCN/AgNi	Calcination	40 mg catalysts 100 mL, 5 mg L ⁻¹	100W W lamp $\lambda \geq 380$ nm	2.24 h ⁻¹	0.028 h ⁻¹	[8]
GCN/AgVO ₃	Hydrothermal	100 mg catalysts 100 mL, 4 mg L ⁻¹	300W W lamp $\lambda \geq 420$ nm	3.54 h ⁻¹	0.014 h ⁻¹	[9]
GCN/In ₂ O ₃	Solvothermal	80 mg catalysts 80 mL, 10 mg L ⁻¹	350W W lamp $\lambda \geq 400$ nm	2.76 h ⁻¹	0.028 h ⁻¹	[10]
CPCN	Calcination	30 mg catalysts 200 mL, 10 mg L ⁻¹	300W Xe lamp $\lambda \geq 400$ nm	1.06 h ⁻¹	0.070 h⁻¹	This work

& The normalized rate (R_n) was estimated by the following equation of: $R_n = r \cdot m_{(\text{RhB})} / m_c$, where $m_{(\text{RhB})}$ is the initial weight of RhB, m_c is the weight of photocatalyst, and r is the rate constant.

Figure S6 Photocatalytic stabilities (A) and XRD patterns before and after photocatalytic reaction of CPCN. It can be observed the XRD peaks intensities of CPCN were obviously shows decreased and some of the peaks were disappeared after six recycling process during the photocatalytic reaction. This is mainly attributed to the following reasons. On one hand, some of the porous microstructure of CPCN are collapses due to the repeated dispersion process in RhB solution by ultrasound during

the photocatalytic process. As such, some CCN grains become smaller and some CPCN flake may be exfoliated. This was confirmed by the SEM image and the broader peaks in the XRD pattern of the CPCN after photocatalytic reaction. On the other hand, owing to the good dispersibility of CPCN in the RhB solution, it is difficult to totally collect all the CPCN for the next photocatalytic experiment. In this case, some CPCN, especially the small-sized CCN, tended to be lost during the cycling experiments since we used a separator member with an average size of about 0.22 μm to separate the photocatalysts from solution every time. Furthermore, a slight corrosion of CPCN may be induced by photogenerated holes.

Figure S7 SEM (A) and the magnified SEM images of CPCN after the photocatalytic reaction.

Figure S8 Trapping experiment of active species during the photocatalytic degradation of RhB.

Figure S9 Mott-Schottky curves of GCN (a) and CCN (b).

Figure S10 Schematic illustrations of the possible charge transfer for photocatalytic degradation over CCN under visible light irradiation.

The above photoreaction mechanism (Type I) is based on the ideal band gap structures of CCN and GCN. In this kind of heterojunction (type I), photoexcited electrons can transfer from GCN to CCN since the CB of GCN is higher than the CB of CCN, while the holes can be transferred from VB (GCN) to VB (CCN) when the contact between GCN and CCN is sufficient. Although the charge carriers (e^-

and h^+) may tend to be accumulated in CCN, this can also improve the photocatalytic performance since the recombination of charge carriers is slower in CCN due to the less conjugated structures. Meanwhile, the CCN is expected to act as an efficient light harvester in the CPCN due to the smaller band gap. As such, there are more holes (h^+) produced in CCN. This allows the possible transfer of holes from the VB of CCN to that of CPCN due to the dynamic reasons and inner electric fields caused by the different VB position. Furthermore, the intimate heterojunction and higher specific surface area ensures effective consumption of charge carriers by photocatalytic degradation for a short carrier transport distance and the exposure of a large surface area. This will also greatly suppress the electron-hole recombination in CCN or CPCN. This photocatalytic reaction mechanism needs to be further clarified in the future since the band gap structure of CCN is highly related to the degree of crystallinity and the compositions (Dontsova, D., et al. 2015, 27, 5170). Different contents of Li and Cl embedding results in the different electronic structures of CCN. As such, the heterojunction type in the CPCN may be different from Figure S10, and Type II heterojunction may also exist in CPCN. This explains that the CPCN prepared with different amount of LiCl exhibited different photocatalytic activity.

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