

# Article

# A Novel Synthetic 3D Interconnected Porous Carbon-Rich Graphitic Carbon Nitride for Boosting Visible Light Photocatalytic Hydrogen Production and Dye Contaminant Degradation

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Abstract: The use of photocatalysis to address environmental pollution and energy shortage is an attractive choice. Herein, we successfully synthesized a novel 3D interconnected porous carbon-rich g-C<sub>3</sub>N<sub>4</sub> catalyst via facile thermal polymerization to enhance photocatalytic hydrogen production and photodegradation of dye contaminants. Enhanced hydrogen evolution (1956.23  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>) and photocatalytic RhB degradation (96.74%) efficiency were achieved with the as-obtained catalysts. Based on the photocatalytic experimental data and characterization analyses, an enhancement mechanism was proposed. The 3D interconnected porous structure endowed the g-C<sub>3</sub>N<sub>4</sub> with numerous active sites and a large specific surface area, and the carbon modification facilitated the separation and transfer of the photoinduced charge carriers. Nanoshape engineering and the carbon-rich structure showed a synergetic effect in increasing photocatalytic performance. This study offers an applicable methodology for the exploitation of an economical catalyst to alleviate environmental pollution and energy shortages.

**Keywords:** photocatalysis; carbon-rich g-C<sub>3</sub>N<sub>4</sub>; contaminant photodegradation; photocatalytic hydrogen production

# 1. Introduction

The environmental pollution and energy crises faced by human beings have become urgent issues related to sustainable development [1–4]. As an efficient, low-energy, and environmentally friendly technology, photocatalysis has emerged as an effective strategy for addressing these two issues [5–8]. To date, photocatalysis has been applied to hydrogen evolution [9], CO<sub>2</sub> reduction [10], pollutant degradation [11], microbial inactivation [12], and so on. Nevertheless, the need for efficient and robust photocatalysts is an important factor restricting the development of photocatalysis. For this reason, researchers have devoted many studies to developing high-efficiency and durable catalysts [13–15].

In this respect, graphitic carbon nitride  $(g-C_3N_4)$  performs very well due to its special electronic band structure, tendency toward stability, and VIS irradiation response [16,17]. However, bulk g-C<sub>3</sub>N<sub>4</sub> still has a series of shortcomings restricting its application, such as a low specific surface area (SSA), limited light absorption (g-C<sub>3</sub>N<sub>4</sub> has a moderate band gap of 2.7–2.8 eV), and rapid recombination rate for photogenerated charges [18,19]. Considerable effort has been devoted to addressing these inherent shortcomings, such as with element doping, structural control, heterojunction construction, and surface modifications [20–23]. Therefore, doping with nonmetallic elements has been deemed an efficient and facile



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strategy for improving photocatalytic performance [12]. This strategy maintains the metalfree nature of g-C<sub>3</sub>N<sub>4</sub> and enhances the efficiency of photoinduced carrier separation, which enhances the photocatalytic activity. To date, many nonmetallic element atoms (such as P, O, B, S, and C) have been successfully doped onto the skeletons of graphitic carbon nitride to increase the photocatalytic efficiency [24–26]. For example, Yu et al. [27] synthesized dual P-doped g-C<sub>3</sub>N<sub>4</sub>, which displayed enhanced photocatalytic H<sub>2</sub>O<sub>2</sub> production. Among these atoms, self-doping is the preferred choice since the introduction of heteroatoms can provide a new center for charge recombination. Moreover, self-doping can change the structure and conductivity of g-C<sub>3</sub>N<sub>4</sub> without introducing other impurity elements, thereby improving its photocatalytic activity. Herein, we prepared C-doped g-C<sub>3</sub>N<sub>4</sub> with significantly improved photocatalytic performance by the dopant of cytosine.

In addition, with an appealing electronic band structure and relatively low recombination rate for the charge carriers, the key factor limiting the photocatalytic activity is the paucity of active sites [17]. Pristine g-C<sub>3</sub>N<sub>4</sub> presents limited photocatalytic activity because of the small SSA and resulting poor solvent dispersibility. In this regard, various g-C<sub>3</sub>N<sub>4</sub> structures, such as 0D nanodots [28], 1D nanoribbons [29], 2D nanosheets [30], and 3D nanospheres [31], have been synthesized to provide additional active sites and promote photocatalytic efficiency. In particular, 2D nanosheets have been prepared due to their large SSA and abundant reactive sites. However, their thinness and smaller particle sizes make them difficult to separate from suspensions, thereby causing secondary pollution [32,33]. However, 3D structural g-C<sub>3</sub>N<sub>4</sub> catalysts assembled on 2D nanosheets maintain a larger SSA and reactive sites while avoiding structural conglutination during the photocatalytic process [34]. Based on these considerations, a combination of nonmetallic element doping and nanoshape engineering strategies may be a conceivable way to modify the photocatalytic efficiency.

In this study, we coupled carbon self-doping with morphological adjustments and fabricated 3D interconnected porous carbon-rich graphitic carbon nitride catalysts with enhanced VIS radiation photocatalytic activity. The 3D porous structure endows  $g-C_3N_4$  with more active sites and adsorption sites, and C doping increases the VIS irradiation response range of the catalyst. The two work together to result in the enhancement of photocatalytic activity. Hydrogen generation via water decomposition and RhB elimination tests were conducted to verify the capability of the as-prepared catalysts. Furthermore, based on characterization analyses and photocatalytic experimental data, a reasonable photocatalytic mechanism was developed.

## 2. Results and Discussion

### 2.1. Morphologies and Structures

The formation mechanism of carbon-rich  $g-C_3N_4$  is shown in Figure S1. In the synthesis process of PCN, the melamine and cyanuric acid would form melamine-cyanuric acid supramolecular (MCS) under magnetic stirring due to the self-assembly effect. The cyanuric acid in the MCS decomposes into gases during the calcination at high temperatures because of its instability, and thus, the 3D interconnected porous  $g-C_3N_4$  catalysts were obtained. In the same way, the MCS came into being in the preparation of PCCN catalysts. At the same time, cytosine is attached to the surface of MCS due to hydrogen bonding. During the calcination at high temperatures, the C atoms from the cytosine ring substituted melamine in the MCS and doped into the  $g-C_3N_4$  framework, forming carbon-rich  $g-C_3N_4$ .

To determine the morphologies and structures of the as-synthesized samples, we used transmission electron microscopy (TEM, JEM-2010, JEOL Co., Ltd., Beijing, China) and field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Tokyo, Japan), and the morphological results are illustrated in Figures 1 and S2). As expected, the BCN samples prepared via directly calcinating melamine displayed a typical tight and large blocky shape and irregular agglomerations (Figure 1a), which was undesirable for photocatalytic reactions. However, the PCN samples obtained by the precursor system of melamine and cyanuric acid exhibited 3D interlinked porous structures, as shown in Figure 1b. The 3D

interconnected structure endowed the g-C<sub>3</sub>N<sub>4</sub> catalysts with stronger adsorption capacity during the photocatalytic reactions and provided abundant active sites to enhance the photocatalytic performance. In addition, the PCCN, fabricated through annealing the supermolecules of melamine, cyanuric acid, and cytosine, still had a 3D interconnected porous structure (Figures 1 and S2). Of note, the 3D interconnected porous structures of PCCN samples became thinner as the cytosine content was increased, which was consistent with the increased SSA (Figure 1a and Table 1). Furthermore, TEM provided more details about the 3D structure characteristics of the 3D interconnected porous form of the unit cross-linking 2D g-C<sub>3</sub>N<sub>4</sub> nanosheet, which was consistent with our previous study [31]. The elemental mapping plotted in Figure 1f,g verified the presence of C and N elements in the PCCN-20 samples.



**Figure 1.** FESEM images of (**a**) BCN, (**b**) PCN, and (**c**) PCCN-20; TEM images of (**d**) PCN and (**e**) PCCN-20; and (**f**) elemental mapping of PCCN-20.

**Table 1.** Specific surface areas and total pore volumes of BCN, PCN, PCCN-10, PCCN-20, and PCCN-30.

Samples	Specific Surface Areas (m $^2$ g $^{-1}$ )	as (m <sup>2</sup> g <sup>-1</sup> ) Total Pore Volumes (cm <sup>3</sup> g <sup>-1</sup> )		
BCN	15.16	0.153		
PCN	69.25	0.506		
PCCN-10	75.08	0.560		
PCCN-20	85.68	0.562		
PCCN-30	76.68	0.518		

Nitrogen adsorption–desorption isotherms were used to characterize the texture and porosity of the as-fabricated catalysts. The results summarized in Figure 2a,b show that all samples presented classical H3-type hysteresis loops, indicating the formation of mesoporous materials [35]. Moreover, the BCN had the lowest SSA of 15.16 m<sup>2</sup> g<sup>-1</sup> (Table 1), which was consistent with the SEM results. Obviously, the PCN prepared by calcination of melamine and cyanuric acid exhibited a greatly increased SSA with a 3D interlinked porous structure, which contained ample active sites and adsorption sites for photocatalytic reactions. Fortunately, the SSAs of the PCCN samples were increased slightly by the addition of cytosine and reached 85.68 m<sup>2</sup> g<sup>-1</sup> under the optimal conditions (PCCN-30), which indicated that the carbon-rich graphitic carbon nitride structure would further increase the SSA of 3D g-C<sub>3</sub>N<sub>4</sub>. Generally, the pore size distribution curves presented in Figure 2b were consistent with the SSA of the catalysts, which verified the effect of the 3D structure and C-doping on the morphology of the catalysts.



**Figure 2.** (a)  $N_2$  isotherms and (b) pore size distribution images of BCN, PCN, and PCCN samples; (c) XRD and (d) FT-IR spectra of BCN, PCN, and PCCN samples; (e) XPS survey spectrum and (f) N 1 s spectrum for PCCN-20; XPS C 1 s spectra of (g) PCN and (h) PCCN-20; and (i) EPR spectra of PCN and PCCN-20.

To understand the crystal structure and surface groups of the as-prepared catalysts, Xray diffraction (XRD, PANalytical, EA Almelo, The Netherlands) patterns along with Fourier transform infrared (FT-IR, NEXUS 470, Nicolet, Wisconsin, US) spectra were recorded. As shown in Figure 2c, two peaks were observed at approximately 27.8° and 12.7° for the (002) and (100) planes of g-C<sub>3</sub>N<sub>4</sub>, which was consistent with the interlayer-stacking of aromatic units and the repeated planar tri-s-triazine (heptazine) units [36], respectively. In addition, the intensity of the diffraction peak centered at 27.8° for the PCCN samples gradually weakened compared with that of the PCN. This indicated that carbon derived from the introduction of cytosine inhibited polymeric condensation of the g-C<sub>3</sub>N<sub>4</sub>. In addition, the FT-IR spectra of the as-prepared samples in Figure 2d exhibited similar absorption peaks at approximately 810 cm<sup>-1</sup>, which were ascribed to a tri-s-triazine bending vibration [35]. Many peaks from 1200 to 1700 cm<sup>-1</sup> arose from stretching vibrations of the CN heterocyclic rings [37], and numerous peaks centered at approximately 3200 cm<sup>-1</sup> were attributed to N–H stretching vibrations [38]. In summary, the XRD and FT-IR results demonstrated that added elements did not destroy the pristine structure of g-C<sub>3</sub>N<sub>4</sub>.

We also used X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical, Manchester, UK) to further analyze the structures and surface groups of the as-synthesized samples, and the results are shown in Figure 2e–h. The XPS survey spectrum for PCCN-20 contained signals for the C, N, and O elements, and the trace amount of O may be attributed to H<sub>2</sub>O or CO<sub>2</sub> adsorbed in the catalyst. As shown in Figure 2f, the N 1 s signal was deconvoluted into four peaks at 398.8, 400.0, 401.3, and 404.5 eV, which were ascribed to C–N=C groups, tertiary nitrogen (N–(C)<sub>3</sub>) groups, C–N–H<sub>x</sub>, and  $\pi$  excitation [39], respectively. In addition, in the C 1 s spectrum of PCCN-20 (Figure 2g), the peaks at 288.3, 286.5, and

284.8 eV were attributed to sp<sup>2</sup> hybridized carbons in N–C=N bonds [40], N–sp<sup>2</sup> carbons in the triazine rings, and carbon impurities, respectively. Additionally, it was noteworthy that the C content in the PCCN-20 catalyst had increased due to the introduction of cytosine (inset image in Figure 2g,h), indicating the successful introduction of carbon. These results are shown more clearly in Table 2, which indicates that the C content of PCCN-20 increased from 47.39% to 48.19%.

Table 2. The contents of C and N in PCN and PCCN-20 catalysts according to the XPS measurement.

Atomic %	С	Ν	0
PCN	47.39%	50.67%	1.93%
PCCN-20	48.19%	49.72%	2.09%

Electron paramagnetic resonance (EPR, MEX-nano, Bruker, Karlsruhe, Germany) was performed to assess unpaired electrons formed by the as-fabricated samples. Obviously, both PCN and PCCN-20 exhibit the same Lorentzian lines located at g = 2.004 (Figure 2i). In addition, PCCN-20 showed a higher single intensity, identifying more delocalized electrons generated from rich carbon [41], which was helpful for the separation of photoinduced charge carriers.

### 2.2. Optical and Electrochemical Performance

UV–VIS diffuse reflectance spectroscopy (UV–VIS DRS, U-3900, Hitachi, Tokyo, Japan) was used to assess the absorption capacity of the as-fabricated catalysts, and the results are illustrated in Figure 3a. All as-prepared samples showed similar spectra with absorption peaks in the VIS radiation region. In comparison with that for PCN, the visible absorption peaks of the as-prepared PCCN catalysts were slightly enhanced, suggesting slightly greater light absorption. In addition, the band gap energy (Eg) was calculated with a Tauc plot, as shown in the inset in Figure 3a [42]. The narrowed band gap energy was consistent with the UV–VIS DRS results, indicating that more charge carriers were generated for the photocatalytic reactions.

It is commonly recognized that charge separation and migration in catalysts are crucial aspects of their photocatalytic capacity. Therefore, steady-state photoluminescence (PL, Fluoromax-4, HORIBA Jobin Yvon, Kyoto, Japan) spectroscopy was used to assess charge separation in the as-prepared samples. As displayed in Figure 3b for PCN, an obvious emission peak at approximately 470 nm was ascribed to band-to-band recombination. Compared with PCN, the PCCN samples showed decreased emission peak intensity, suggesting a significantly suppressed combination of the photoinduced charge carriers. Time-resolved photoluminescence (RTPL, FLSP920, EI, Edinburgh, UK) decay spectra (Figure 3c) were also obtained, and they supplied more detail on the photogenerated charge carriers, from which the average recovery lifetimes ( $\tau$ ) were derived, as in Equation (1) [43]. Apparently, PCCN-20 (5.84 ns) showed a longer emission lifetime than PCN (5.14 ns), which was displayed in Table 3, indicating that the doped carbon enhanced the migration of the photogenerated charge carriers.

$$(\tau) = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{1}$$

Decay Time (ns)		Relative Amplitude		Average
$\tau_1$	$\tau_2$	A <sub>1</sub>	A <sub>2</sub>	Lifetime (ns)
2.14 1.94	8.17 8.17	400.89 326.06	104.08 130.44	5.14 5.84
	Decay T τ <sub>1</sub> 2.14 1.94	Time (ns)   τ1 τ2   2.14 8.17   1.94 8.17	Decay Time (ns) Relative A   τ1 τ2 A1   2.14 8.17 400.89   1.94 8.17 326.06	Decay Time (ns) Relative Amplitude   τ1 τ2 A1 A2   2.14 8.17 400.89 104.08   1.94 8.17 326.06 130.44

Table 3. Lifetime profile and corresponding carrier dynamics information of the PCN and PCCN-20.

The charge-transfer efficiency of the catalysts was obtained with electrochemical impedance spectroscopy (EIS), as illustrated in Figure 3d. Based on the equivalent circuit model, PCN and PCCN-20 had the highest and smallest EIS Nyquist arc radii, respectively, indicating the worst and best charge separation and transfer capacities [44].



**Figure 3.** (a) UV–VIS DRS and Tauc's plot of PCN and PCCN-20 (inset), (b) PL, (c) RTPL spectra, and (d) EIS of BCN, PCN, and PCCN catalysts.

### 2.3. Photocatalytic Capacity for H<sub>2</sub> Production and RhB Degradation

To assess the photocatalytic activity of the as-fabricated catalysts, catalytic water splitting experiments were performed with irradiation in the VIS radiation region ( $\lambda > 420$  nm). Figure 4a shows that the BCN with a blocky shape displayed poor reactivity and released only 119.21 µmol g<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub> within 1 h. Due to the 3D interconnected structure, the H<sub>2</sub> evolution yield for PCN reached 765.06 µmol g<sup>-1</sup> h<sup>-1</sup>, which was 6.42 times that of BCN, suggesting that the 3D interconnected structure significantly enhanced the photocatalytic capacity. For the PCCN catalysts, the H<sub>2</sub> evolution rates were substantially higher than that of PCN, strongly confirming that the carbon-modified 3D porous g-C<sub>3</sub>N<sub>4</sub> enhanced the photocatalytic capacity. In particular, PCCN-20 exhibited a significantly enhanced H<sub>2</sub> production rate of 1956.23 µmol g<sup>-1</sup> h<sup>-1</sup>, which was approximately 16.41 times and 2.56 times those of the BCN and PCN samples, respectively. Nevertheless, the decreased H<sub>2</sub> production efficiency with the excessive carbon doping (from 1956.23 µmol g<sup>-1</sup> h<sup>-1</sup> to 1701.07 µmol g<sup>-1</sup> h<sup>-1</sup>) may be attributed to the generation of more recombination centers for the photogenerated charge carriers.

In addition, long-term photocatalytic stability is necessary for practical applications [45]. Therefore, we used a cycling experiment to probe the persistence and reusability of the as-synthesized catalysts. The as-synthesized rich-carbon PCCN-20 catalysts still showed H<sub>2</sub> evolution yields of 1890.34  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> after 15 h of consecutive continuous photocatalytic H<sub>2</sub> evolution (Figure 4c). However, the slight decrease in the H<sub>2</sub> evolution rate may have resulted from a slight loss of the PCCN-20 catalyst during the washing process. The



conclusion was reached from the cycling results showing that the as-synthesized catalysts showed outstanding stability and reusability.

**Figure 4.** (a)  $H_2$  production and (b) the corresponding production rate of the as-synthesized catalysts; (c) stability of the PCCN-20 catalysts during  $H_2$  production; (d) degradation rate and (e) corresponding k values for RhB degradation in different conditions; and (f) stability of RhB degradation by PCCN-20 catalyst.

Rhodamine B (RhB), a synthetic dye, is widely used in the textile printing and food industries and has carcinogenicity. It is one of the common pollutants in industrial wastewater because of its solubility and good stability [46]. However, its toxicity, carcinogenicity, and mutagenicity make it an urgent issue to remove it from wastewater. Therefore, using RhB as a probe pollutant, we performed pollutant degradation experiments to appraise the photocatalytic activity of the as-synthesized catalysts. Figure 4d displays the concentration of RhB as a function of irradiation time in the presence of different catalysts. The first-order kinetic equation (Equation (2)) was used to simulate the degradation process [47], in which  $C_0$  is the initial RhB concentration, and C is that at time t (min).

$$\ln\left(\frac{Ct}{C_0}\right) = -kt \tag{2}$$

First, we can notice that the degradation of RhB without a catalyst can be negligible (only 3.2% within 15 min). BCN showed the slowest degradation rate (10.32% within 15 min) with a k value equal to 0.007 min<sup>-1</sup>, and PCN showed a higher degradation efficiency of 70.43% within 15 min. As with the H<sub>2</sub> evolution results, the PCCN catalysts showed significantly higher RhB degradation rates. The RhB degradation rates for the PCCN-20 catalysts reached 96.74% within 15 min of VIS radiation irradiation, and the k value (0.228 min<sup>-1</sup>) was approximately 32.57 times and 2.81 times those of BCN (0.007 min<sup>-1</sup>) and PCN (0.081 min<sup>-1</sup>), respectively. However, additionally, the cycling experiments verified the good stability and reusability of the PCCN-20 catalyst in RhB photodegradation. These results for H<sub>2</sub> evolution and RhB degradation proved that the morphology and carbon-rich g-C<sub>3</sub>N<sub>4</sub> structure showed synergism in enhancing photocatalytic performance.

It is widely accepted that photogenerated active species such as hydroxyl radicals ( $^{\circ}OH$ ) and superoxide radicals ( $O_2^{\circ-}$ ) are involved in contaminant degradation. They can be generated by the following reactions (Equations (3)–(8)):

PCCN catalyst + hv 
$$\rightarrow$$
 h<sup>+</sup> + e<sup>-</sup> (3)

$$2e^{-} + O_2 + 2H^+ \rightarrow H_2O_2$$
 (4)

$$H_2O_2 + e^- \to \bullet OH + OH^-$$
(5)

$$e^- + O_2 \to O_2^{\bullet -} \tag{6}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{7}$$

$$h^{+} + OH^{-} \to {}^{\bullet}OH \tag{8}$$

Therefore, radical quenching experiments were used to further explore the contributions of generated active substances, where  $h^+$ ,  $O_2^{\bullet-}$ , and  $\bullet$ OH were captured by the trapping agents EDTA-Na<sub>2</sub>, BQ, and IPA [48], respectively. As shown in Figure 5a,b, the various scavengers showed different degrees of inhibition for the photocatalytic degradation of RhB by PCCN-20. The degradation rates were slightly suppressed by the presence of EDTA-Na<sub>2</sub> and IPA, from 96.74 to 81.88 and 77.51% (the k values were reduced from 0.228 to 0.114 and 0.100 min<sup>-1</sup>), respectively, indicating that  $h^+$  and  $\bullet$ OH participated in RhB degradation. The efficiency for the removal of RhB showed a dramatic decline after adding BQ, reaching 52.20%, which suggested that  $O_2^{\bullet-}$  played an irreplaceable role in the process of RhB degradation by PCCN-20.



**Figure 5.** (a) RhB degradation rates in the radical quenching experiments and (b) the corresponding k values.

# 2.4. Mechanism of Enhanced Photocatalytic Activity

Based on the photocatalytic experimental data and characterization analyses, a photocatalytic mechanism was developed in this study (Figure 6). Under VIS radiation, electrons in the VB of the PCCN catalysts were promoted to the CB, leaving holes in the VB and resulting in the separation of the photogenerated charge carriers. The photogenerated holes were transferred to the surface of the catalysts and participated in RhB degradation, while the photoinduced electrons were transported to the surface and participated in hydrogen evolution. During the whole process, the 3D interconnected porous structure of  $g-C_3N_4$  provided copious active sites and a large SSA, and the carbon-rich  $g-C_3N_4$ structure facilitated the separation and migration of the photogenerated charge carriers, thus resulting in enhanced RhB degradation efficiency and hydrogen evolution rate. In summary, nanoshape engineering and carbon doping had a synergetic effect in promoting photocatalytic performance.



**Figure 6.** Potential mechanism of hydrogen generation with water decomposition and RhB elimination by PCCN-20.

# 3. Materials and Methods

# 3.1. Materials and Reagents

The analytical reagent (AR) melamine, cyanuric acid, cytosine, and rhodamine B (RhB) were purchased from Shanghai Maclin Biochemical Co., Ltd. (Shanghai, China). In addition, other chemical reagents, including ethylene diamine tetraacetic acid disodium salt (EDTA-Na<sub>2</sub>), isopropanol (IPA), and benzoquinone (BQ), were purchased from Sigma-Aldrich (St. Louis, MO, USA). All reagents were used directly without further purification.

# 3.2. Fabrication of the Catalysts

Figure 7 displays the synthetic procedure used to prepare the catalysts. All of the  $g-C_3N_4$  catalysts were synthesized through simple calcination.



Figure 7. Synthetic procedure for the PCCN, PCN, and BCN samples.

# 3.2.1. Synthesis of BCN

Bulk g-C<sub>3</sub>N<sub>4</sub> (denoted as BCN) catalysts were synthesized by annealing melamine at 550 °C for 4 h (with a ramping rate of 2 °C min<sup>-1</sup>) directly.

# 3.2.2. Preparation of PCN

The 3D interlinked porous g-C<sub>3</sub>N<sub>4</sub> catalysts were prepared through simple calcination. Typically, 1.26 g of melamine and 1.29 g of cyanuric acid were dissolved in distilled water (100 mL) and stirred magnetically for 10 h. The product was dried at 60 °C, and it was calcined at 550 °C for 4 h (with a ramping rate of 2 °C min<sup>-1</sup>). The resulting faint yellow powder was the 3D interconnected porous g-C<sub>3</sub>N<sub>4</sub> catalyst.

### 3.2.3. Preparation of PCCN

The 3D interlinked porous  $g-C_3N_4$  catalysts were prepared by the same synthesis method as PCN; the only difference was that the precursors of PCCN were 1.26 g of melamine, 1.29 g of cyanuric acid, and a certain amount of cytosine. The as-synthesized 3D interconnected porous carbon-rich  $g-C_3N_4$  samples with 10, 20, and 30 mg of cytosine were labeled PCCN-10, PCCN-20, and PCCN-30, respectively.

## 3.3. Characterization Measurements

X-ray diffraction (XRD) patterns of the catalysts were collected on a Holland Panalytical PRO PW3040/60. The surface chemical status of the samples was characterized by X-ray photoelectron spectroscopy (XPS, Kratos-AXIS ULTRA DLD, and Al K $\alpha$  X-ray source). The morphologies and structures of the prepared samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL Co., Ltd, Beijing, China). UV-Vis diffuse reflectance spectra (DRS) of the as-prepared samples were obtained by a Hitachi U-3900 spectrophotometer (Tokyo, Japan). The room temperature photoluminescence (PL) spectra were examined by fluorescence spectrophotometer (HORIBA Jobin Yvon fluoromax-4, Kyoto, Japan) with an excitation wavelength of 385 nm. The time-resolved PL (RTPL) spectra were recorded by a Multifunction Steady State and Transient State Fluorescence Spectrometer (FES920, Edinburgh Instruments, Edinburgh, UK) at 300 nm. The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-max nitrogen adsorption apparatus (Micrometitics, Norcross, GA, USA). The photocurrent was measured on an electrochemical workstation (CHI760E) with a standard three-electrode configuration. Catalyst (10 mg)-loaded indium tin oxide (ITO) electrodes ( $6 \times 6$  mm) served as the working electrode, a Pt foil as the counter electrode, and an Ag/AgCl electrode as the reference electrode under Xe light irradiation in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. EIS was performed over a frequency range from 0.1 Hz to 1 MHz at open-circuit potential in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution under Xe light irradiation.

## 3.4. Photocatalytic Measurements

Hydrogen generation with water decomposition and RhB elimination tests were executed under VIS radiation irradiation to estimate the capability of the as-prepared samples.

Photocatalytic H<sub>2</sub> evolution was conducted using a photocatalytic analysis system (Labsolar 6A, Perfectlight, Technology Co., Ltd, Beijing, China). VIS radiation was obtained from a 300 W Xe lamp with a 420 nm cutoff filter. Amounts of 50 mg of photocatalysts were added into 100 mL solution (90 mL deionized water and 10 mL triethanolamine as sacrificial agent). Amounts of 1wt.% Pt as co-catalysts were loaded on the photocatalysts by in situ photo-deposition method using H<sub>2</sub>PtCl<sub>6</sub>. Before light irradiation, the suspensions were ultrasonically dispersed in the dark for 30 min to achieve absorption–desorption equilibrium. At given time intervals (30 min), a certain amount of produced gas was measured by an online gas chromatograph (GC-2002 N/TFF) equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using argon as the carrier gas.

Product gases were calibrated with standard  $H_2$  gas, and their identities were determined according to the retention time.

The catalytic performance of catalysts was evaluated by degradation of RhB. All reactions were carried out in a photochemical reactor (Yanzheng Co., Ltd., Shanghai, China) with condensed water under stirring. A 500 W metal halide lamp with a 420 nm cutoff filter (average light intensity:  $30 \text{ mW cm}^{-2}$ ) was used as the light source. Briefly, 40 mg of catalyst was ultrasonically dispersed into organic contaminant solution (80 mL,  $20 \text{ mg L}^{-1}$ ), then stirred in darkness for 30 min to achieve an adsorption–desorption balance between catalyst and RhB. During catalytic reaction, 3 mL of suspension was taken out at given time intervals and immediately centrifuged to remove the catalyst. The filtrate of RhB was determined with a Hitachi U-3900 UV-vis spectrophotometer, and the absorbance value of RhB was used to calculate the concentration at the maximum absorption wavelength.

### 4. Conclusions

In this study, combining morphological control and carbon doping, we successfully synthesized a novel 3D interconnected porous carbon-rich  $g-C_3N_4$  catalyst via facile thermal polymerization. The obtained catalysts of PCCN-20 showed the best photocatalytic performance with a 96.74% RhB degradation efficiency and a 1956.23 µmol  $g^{-1}$  h<sup>-1</sup> hydrogen evolution rate, which were approximately 2.81 and 2.56 times that of PCN. However, the photocatalytic capacity of PPCN catalysts declined with the decrease in cytosine addition, indicating that the addition of excessive C element would lead to a photogenerated charge recombination center, which would affect the photocatalytic performance. Moreover, the mechanistic analysis showed that morphological control and carbon doping had a synergetic impact in enhancing photocatalytic performance. In a word, this research offered a possible and imputable reference for the development of economical catalysts for alleviating environmental pollution and energy shortages.

**Supplementary Materials:** The following supporting information can be downloaded at https://www. mdpi.com/article/10.3390/catal13101345/s1. Figure S1: The schematic copolymerization processes of PCCN from melamine, cyanuric acid and cytosine; Figure S2: The SEM images of (a) PCCN-10 and (b) PCCN-30.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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