Distorted polymeric carbon nitride via carriers transfer bridges with superior photocatalytic activity for organic pollutants oxidation and hydrogen production under visible light

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Abstract

Polymeric carbon nitride (PCN) has become the most promising metal-free photocatalysts but its activity is low. Molecule doping of PCN has been proved to be an effective strategy to achieve high photocatalytic performance. Herein, we report a bottom-up method to synthesize modified PCN, which includes 2,5-dibromopyrazine doping, thermal-induced exfoliation and condensation/polymerization. The incorporation of electron-deficiency 2,5-dibromopyrazine into the PCN framework can effectively tune the electronic structures and improve the charge-carrier separation. In addition, the incorporation of 2,5-dibromopyrazine induced significant structural changes from planar symmetric to distortion. The optimized pyrazine doped PCN showed a reaction rate enhancement of 4-fold for the degradation of sulfamethazine compared to that of conventional urea-based PCN. Further reactive species and degradation intermediate detection studies, indicated that $\bullet O_2^-$ was generated during the photocatalytic process, which could lead to the decomposition, and finally mineralization of sulfamethazine. 2,5-Dibromopyrazine doped PCN also leads to a 6.3-fold improvement in H_2 generation with the visible light. Especially, phytotoxicity experiments showed that the toxicity of sulfamethazine after degradation is greatly reduced, and the as-prepared photocatalyst is environmentally friendly.

Key words: Polymeric carbon nitride; 2,5-dibromopyrazine; Carrier channel; Photocatalytic H_2 evolution; Sulfamethazine degradation.

1. Introduction

In recent years, micro-pollutants (i.e. antibiotics and endocrine disrupting chemicals) in aquatic environments have attracted increasing concerns [1, 2]. Sulfamethazine (SMZ) is a typical sulfonamide antibiotic that is intensively used in medicine, aquaculture, livestock and poultry farming [3, 4]. Studies indicated that about 30%-90% of sulfonamides drugs or its metabolites are released through urine and excrement into the surface and subsurface water bodies, which can become a potential risk to human health [5, 6]. Photocatalytic water treatment as a green and sustainable advanced oxidation process has great potential in removing organic pollutants from wastewater [7-10]. On the other hand, photocatalytic water splitting has been regarded as a sustainable way to solve the energy crisis [11, 12]. Therefore, it is urgent to explore effective and stable photocatalyst for hydrogen evolution reaction and water purification. In the past decades, many semiconductor materials, such as TiO_2, CdS, Bi_2WO_6, $Bi_{12}O_{17}Cl_2$ and polymeric carbon nitride (PCN), have been explored for photocatalytic reactions under UV and visible light irradiation [13-19].

Among these novel photocatalysts, PCN has attracted much attention due to the suitable band structure and the appropriate optical absorption [20-25]. It also exhibits excellent chemical stability. PCN has been extended studied in photocatalytic degradation, water splitting and inactivation of microorganism due to its low cost and nontoxicity characters [26-30]. However, PCN as a typical polymer, the local structure was rather disordered and the exciton binding energy was high, leading to the insufficient separation of charge carriers. Moreover, the light adsorption edge of pristine PCN is below 460 nm. So, the photocatalytic application of PCN has been limited by these above demerits [31, 32]. Enormous efforts have been explored to improve the photocatalytic activity of PCN, which including element doping, coupling with other semiconductors, and molecular doping copolymerization [33-38]. Especially, molecular copolymerization is a unique and effective method that can modify the structure and properties by introducing organic molecules into the PCN framework.

Recently, copolymerizing similar aromatic structure with PCN precursors has been a typical molecular assembly method to extend the π electrons of the PCN aromatic system and modulate the electronic band structure, leading to affect its photocatalytic activity [39-42]. Some organic molecules have been employed to dope into PCN like benzene-based molecules, thiophene-based molecules and nitric heterocyclic-based molecules and many more [43-47]. Yan et al. developed aromatic ring substituting doping PCN by using urea and 2, 4, 6-trichlorophenol as the precursors [48]. The hydrogen evolution rate (HER) of modified PCN reached as high as 12.543 mmol h^{-1} g^{-1}, which is higher than that of pristine CN (1.071 mmol h^{-1} g^{-1}). Li et al. prepared pyrimidine-doped PCN by using urea and 2, 4-diaminopyrimidine as co-monomers [49]. The extended light adsorption and the enhanced charge transport of pyrimidine-doped PCN resulted in the enhancement of HER activity (from 0.46 mmol h^{-1} g^{-1} to 2.8 mmol h^{-1} g^{-1}). However, it should be noticed that the research studies focused on limited skeletal structures (i.e. aromatic, pyrimidine) and applied in HER, more heterocyclic structure like pyrazine chemicals should be explored. Pyrazine and its derivatives have been used as acceptor co-monomers in donor-acceptor semiconducting polymeric materials. Therefore, it was expected that molecular doping of the PCN framework via integrating pyrazine is a feasible strategy to modify its surface properties and charge carriers transfer, which may leads to the positive effect on photocatalytic reactions.

In this context, urea and 2,5-dibromopyrazine was chosen as the precursors for prepared pyrazine-modified PCN photocatalysts (denoted as PCN-DP). Compared with other precursors, urea-derived PCN has a high degree of polymerization and shows the best photocatalytic performance. The dibromo group in 2,5-dibromopyrazine as the co-monomer was able to react with urea and then incorporated into the PCN framework. After incorporating 2,5-dibromopyrazine into the framework of PCN, the PCN-DP sample exhibited enlarged visible light absorption range, suppressed electron-hole recombination rates and promoted charge transfer, which endows them as an excellent candidate for photocatalytic oxidation of organic pollutants and hydrogen evolution. In addition, the phytotoxicity of the wastewater (before and after photocatalytic treatment) and photocatalysts were evaluated to illustrate the toxicity of the degradation products and photocatalysts to the plants as this relates to the reuse of water.

2. Experimental section

2.1 Catalysts preparation

The typical bulk carbon nitride was obtained by a traditional polymerization as reported previously [35]. Typically, 10 g of urea (99%, AR) were added into a ceramic crucible with a cover and heated to 550 ℃ with a heating rate of 5 ℃ min^{-1} and kept for 2 h in air condition. The obtained product was then further heated to 550 ℃ for another 2 h with a ramp rate of 10 ℃ min^{-1}. After cooling to room temperature, the obtained product was washed with distilled water. The yellow powders was further dried at 70 ℃ and denoted as PCN.

The PCN-DP samples were prepared from bottom-up method by thermal-induced exfoliation and polymerization. Typically, 10.0 g of urea and a series of 2, 5-dibromopyrazine (0.1 g, 0.2 g, and 0.4 g) were fine mixed in 3 mL ethanol by ball milling. The obtained mixed precursors were put into a ceramic crucible with a cover and heated to 550 ℃ with a heating rate of 5 ℃ min^{-1} and kept for 2 h in air. The obtained product was then further heated to 550 ℃ for another 2 h with a ramp rate of 10 ℃ min^{-1}. The final product was dried at 70 ℃ after water wash and denoted as PCN-DP-x, where x indicates the amount of DP (x=0.1 g, 0.2 g, and 0.4 g).

2.2 Characterization

The crystal phase of samples were investigated by Rigaku D/max-2500 X-ray diffraction (XRD) with Cu *Kα* radiation (λ = 0.15406 nm). The morphology of samples was collected by scanning electron microscopy (SEM, FEI Helios NanoLab 600i) and transmission electron microscopy (TEM, FEI tecnai G2F20 electron microscope). Fourier transform infrared spectroscopy (FTIR) spectra were measured on BIORad FTS 600 spectrometer in the range of 500-4000 cm^{-1}. The chemical states were obtained at X-ray photoelectron spectra (XPS, ESCALAB 250Xi). The light absorption was analyzed on UV-vis diffuse reflectance spectra (DRS, Cary 300). Steady room temperature photoluminescence (PL) spectra were conducted in a Perkin Elmer luminesence spectrometer (LS 50 B) with the excitation wavelength of 365 nm. The electron paramagnetic resonance (EPR) of solid and liquid samples was performed on Bruker ER200-SRC spectrometer.

2.3 Photocatalytic performance evaluation

The photocatalytic system was set up in a photochemical reactor under visible light irradiation. The model pollutant used was sulfamethazine (SMZ) [50]. A typical sequence test contained 25 mg catalyst and 10 mg L^{-1} SMZ in 50 mL of water solution. The mixed solution was stirred without light for 1 h to obtained the adsorption and desorption equilibrium. Then, the reactor was irradiated by a 300 W Xenon lamp with a 420 nm cutoff filter. 1 mL suspension was extracted from the reactor in every 15 min and centrifuged at a certain amount of time. The concentration of SMZ was detected by high-performance liquid chromatography (HPLC, Agilent 1260 infinity) with the C_{18} column (4.6 × 150 mm). The HPLC analysis was carried out using an eluent of water and acetonitrile (65:35, v/v) for SMZ. The flow rate of eluent was 1 mL min^{-1} and the detection wavelength was set as 265 nm. The analysis of degradation products was detected by high-performance liquid chromatography-mass spectra (HPLC-MS) and the method was listed in Text S1. In addition, the photocatalytic hydrogen evolution tests were detailed in Text S2.

2.4 Photoelectrochemical measurement

The PCN and PCN-DP electrodes were prepared by drop-coating method . 3 mg of catalyst was dispersed in 1 mL of 0.5% Nafion-ethanol solution, and then the solution was under sonication for 2 h. The obtained mixture was dropped onto the clean F-doped tin oxide (FTO) glass with an effective area of 1 cm × 1 cm. The electrode was then put into muffle furnace for 2 h calcination at 130 ℃. After cooling to room temperature, the working electrodes, the Pt plate electrode (40 × 0.55 mm, 99%), and the Ag/AgCl electrode were immersed in 0.2 M Na_2SO_4 aqueous solution in a three-electrode cell. The test was performed on a CHI 660D workstation. The visible light was offered by a 300 W xenon lamp with a 420 nm cutoff filter. The photocurrent responses of the samples upon light on and off were measured. Electrochemical impedance spectroscopy (EIS) was performed in 100 mL of 0.2 M Na_2SO_4 aqueous solution with 0 V of applied voltage. A Mott-Schottky plot was obtained at a frequency of 900 and 1000 Hz.

2.5 Phytotoxicity test

The phytotoxicity of samples was determined by seed germination and radicle elongation tests with Chinese cabbage (*Brassica rapa* L.) seeds according to the methods of Luo et al [51]. Five samples were tested, which including pure water, SMZ solution (10 mg L^{-1}, before photocatalytic), SMZ solution (10 mg L^{-1}, after photocatalytic), PCN solution (1 g L^{-1}) and PCN-DP-0.2 (1 g L^{-1}), respectively. Pure water was used as the control in the tests. After the surface of seeds being cleaned, 160 individuals were put onto a piece of paper wetted by 5 mL samples in a 90-mm Petri dish for a time. They were kept in an incubator at 25℃ in the dark. After the first incubation stage (24 h), the germinated seeds were recorded to calculate the seed germination rate. And then 20 germinating seeds with similar sizes were selected and then transferred to a new plate containing the same samples for four times. After another 24 h, the radicle length was measured.

3. Results and discussion

3.1 Photocatalyst characterization

Typically, PCN was obtained from urea, while PCN-DP-x was prepared from urea and 2, 5-dibromopyrazine (x represents the mass of 2, 5-dibromopyrazine, ranging from 0.1 to 0.4 g). The XRD patterns of PCN and PCN-DP-x samples are shown in Fig. 1a. The typical XRD peaks at 13.2 ° and 27.7 ° corresponding to (100) inter-planar packing of *s*-triazine units and (002) interlayer stacking were obtained for PCN and PCN-DP-x [52]. Compared with PCN, the intensity of two peaks for PCN-DP was weakened, suggested that the long-range order in atomic arrangements has been destructed by molecular doping and re-calcination [53]. Moreover, the results of FT-IR (Fig. 1b) further confirmed the molecule doping of pyrazine. The FT-IR bands at 1200-1600 cm^{-1}, 810 cm^{-1} can be ascribed to the distinctive aromatic C-N heterocycles and triazine units of PCN [41, 54, 55]. High resolution FT-IR was recorded for PCN and PCN-DP samples (Fig. 1c). Among those peaks, typical peak of PCN likes 1510 cm^{-1} gradually towards the longer wavenumber with the increased addition of pyrazine. It could be caused by an interaction between the pyrazine group and the intrinsic structure of PCN [56, 57].

Organic elemental analysis (OEA) was performed to confirm the introduction of DP in carbon nitride framework (Table S1). It was expected that the C/N atomic ratio would be increased slightly if the DP incorporated successfully. The C/N atomic ratio of PCN-DP-0.2 slightly increased by contrast to PCN (from 0.65 to 0.68). In order to further study the local binding chemical environments of PCN and PCN-DP samples, XPS analyses were carried out. Carbon, nitrogen, and little amounts of oxygen were observed in the spectra of PCN-DP-0.2 (Fig. 1d). Of notice was the absence of bromide characteristics that indicated successful elimination of copolymerization. The C 1s and N 1s of PCN and PCN-DP-0.2 are exhibited in Fig. 1e and f, respectively. The C 1s of samples could be separated into two peaks at 288.3 and 284.7 eV. These peaks were assigned to the N-C=N bonds and the C-C bonds. After pyrazine doping, the percentage of C-C bonds to all carbon increased from 4.0% (PCN) to 12.6% (PCN-DP-0.2), which indicated that other carbon source had incorporated into the carbon nitride system [58]. On the other hand, the N 1s spectra were fitted into three major peaks at 398.4, 399.8, and 400.9 eV, which correspond to C-N=C for the s-triazine, the tertiary nitrogen, and the C-N-H bonds, respectively [59]. A slightly increased of C/N atomic percentage from 0.74 for PCN to 0.79 for PCN-DP-0.2 was also identified by XPS (Table S1), indicating that pyrazine ring has been incorporated in PCN framework successfully.

The morphology change of PCN and PCN-DP-0.2 can obtain by SEM and TEM, as shown in Fig. 2. PCN showed a smooth sheet-like morphology (Fig. 2a), while PCN-DP samples exhibited coral-like and hierarchical network structure (Fig. 2b, 2c and 2d). These results show that the incorporation of a small amount of DP could change the morphology of PCN. The distortion structure in PCN-DP samples allow more n-π* transitions from the edge nitrogen atoms to the conduction band, which might also benefit for the visible photon absorption. In addition, the EDS of PCN-DP-0.2 show the distribution of C and N with trace amount of Br (Fig. S1). The TEM image further indicated the nanosheet-like and pore structural of PCN-DP-0.2. Fig. 2e exhibits that the PCN sample is composed of several thin layers. Fig. 2f and Fig. S2 illustrates that the similar thin layer of PCN-DP-0.2 sample with some irregular pores (the average diameter was 8.9±2.7 nm). The thin layer and porous structure of PCN-DP-0.2 are beneficial to the absorption of light, provide more reactive reaction sites for the reactive species, and improve the photocatalytic activity. N_2 adsorption-desorption measurements further supported the structural changes in PCN-DP materials. Moreover, it was found that all samples matched mesoporous structures due to the typical IV behaviors with H1 type hysteresis loops (Fig. S3). The specific surface areas are 82.87, 89.96, 76.45, and 71.39 $m^2 g^{-1}$ for PCN, PCN-DP-0.1, PCN-DP-0.2, and PCN-DP-0.4, respectively. It can be found that the moderate doping of DP can improve the surface area of PCN. However, when further increasing amount of DP, the specific surface area of PCN-DP-x were decreased. This is mainly because excessive DP may destroy the inherent structure units of PCN and cause pore collapse, which could be examined by the reduction of pore volume from 0.48 to 0.35 cm^3 g^{-1} (Table 1).

The solid-state ^{13}C nuclear magnetic resonance (NMR) spectra of PCN, and PCN-DP-0.2 (Fig. 3a) exhibited two strong peaks at 156.6 and 164.5 ppm, which corresponded to the C-$(N)_3$ group and NH_2-$C(N)_2$ group in the heptazine units, respectively [60]. Interestingly, a peak at 163.0 ppm in the ^{13}C NMR spectra was found in PCN-DP-0.2 sample, which indicated carbon entities are hindered. This distinct signal change indicates that the local chemical environments of carbon nitride are changed and the structural of PCN-DP-0.2 is not symmetric [61]. Moreover, the electronic band structure of catalysts was studied by EPR spectra. As shown in Fig. 3b, PCN and PCN-DP-0.2 showed a paramagnetic absorption signals centered at a *g* value of 2.0036 in the magnetic field of 3260 to 3360 G, which was attributed to the presence of unpaired electrons in carbon nitride and an electron trapped on defects [52, 62]. The EPR signals of PCN-DP-0.2 was higher than PCN, indicating the concentration of unpaired electrons of PCN can be increased by pyrazine doping [63, 64]. This result may also be due to defects caused by the doping of pyrazine.

It was expected that the incorporation of pyrazine into PCN might bring the modification of optical response. UV-Vis diffuse reflection spectra of the PCN and PCN-DP-x samples are shown in Fig. 3c. The adsorption edge of PCN was around 460 nm, which originated from the π-π* electron transitions in the conjugated aromatic ring system. With the incorporation of DP, there are slight absorption tails in the range of 460~700 nm. The absorption tail gradually enhanced with the increased addition of DP. This new band may ascribed to the n-π* electron transition involving the lone pairs [65]. Besides, the color change from yellow to brown suggested that the band gap was changed in PCN-DP samples. The band gap energy of PCN and PCN-DP-0.2 samples were measured to be 2.64 eV and 2.53 eV according to the Tauc plots (inset Fig. 3c), respectively. This reduced band gap of PCN-DP-0.2 indicated that this material effectively harvest wide range of visible light to produce more photogenerated charge carriers. This above change indicates that the introduction of pyrazine group can effectively improve visible light absorption and enhance the concentration of unpaired electrons, leading to the improved photocatalytic activity.

In addition, the conduction band position and valence band position are important for photocatalytic reaction. The flat band potential was measured by Mott–Schottky plots. As shown in Fig. 3d and 3e, the flat band potential (E_{fb}) of PCN and PCN-DP-0.2 were -1.41 V and -1.28 V vs. Ag/AgCl. Through the Nernst equation conversion, the E_{fb} of PCN and PCN-DP-0.2 were -0.86 eV and -0.73 eV vs. NHE [66]. Therefore, the conduction band of PCN and PCN-DP-0.2 were -1.16 eV and -1.03 eV. According to the band gap value, the valence band position of PCN and PCN-DP-0.2 were 1.48 eV and 1.5 eV. The band structure of PCN and PCN-DP-0.2 was given in Fig. 3f. It can be seen that the pyrazine coupling has effectively induced down-shift of VB position and CB position, respectively, thus decreasing the band gap energy. Although the CB position of PCN-DP-0.2 was decreased, but it still has enough reduction potential to induce the photocatalytic reaction.

3.2 Photocatalytic activity

To evaluate the validity of pyrazine doping strategy over PCN on improving photocatalytic activity, photocatalytic degradation of sulfamethazine (SMZ) were carried out over as-prepared samples. SMZ was chosen as the model pollutant since the SMZ is not photolyzed by visible light [67-69]. Our previous studies indicated that the adsorption capacity of carbon nitride for SMZ was negligible [43, 62]. The control experiments and PCN samples were performed in Fig. 4a. When the mass of DP was 0.2 g, 99% of SMZ could be degraded by the PCN-DP-0.2 under visible light irradiation in 60 min. By contrast, the pristine PCN only degraded 75% of SMZ under the same condition. The corresponding pseudo-first order kinetic curve is exhibited in Fig. 4b. The apparent SMZ removal rate constants for PCN, PCN-DP-0.1, PCN-DP-0.2, and PCN-DP-0.4 were 0.023 min^{-1}, 0.051 min^{-1}, 0.087 min^{-1} and 0.065 min^{-1}, respectively. The degradation rate for PCN-DP-0.2 was about 4 times than that of the PCN. After normalized with their BET specific surface areas, the activity of PCN-DP-0.2 (1.14 mg min^{-1} m^{-2}) was still higher than those of PCN (0.27 mg min^{-1} m^{-2}), PCN-DP-0.1 (0.57 mg min^{-1} m^{-2}), and PCN-DP-0.4 (0.91 mg min^{-1} m^{-2}) [70]. Moreover, compared with some existing photocatalysts (i.e. Bi_2WO_6, $Bi_2O_{17}Cl_2$, g-C_3N_4), the PCN-DP-x generally showed excellent photocatalytic activity (Table S2).

Liquid chromatography-mass spectrometer (LC-MS) was used to identify the degradation products of SMZ and two major intermediates were found. The LC spectra indicated that the peak intensity of SMZ (t=9.427 min) was decreased with the reaction time prolonging (Fig. 4c). The peak at 1.229 min and 2.283 min may be attributed to the degradation intermediates of SMZ. Detailed MS graph was provided in Fig. S4. As shown in Fig. 4d, the product ion at *m/z* 279 was the SMZ. The one intermediate P1 was *m/z* 215, corresponding to 4-(2-imino-4,6-dimethylpyrimidin-1(2*H*)-yl) aniline. This product was generated by smiles-type rearrangement followed by SO_2 extrusion[71]. Recent studies have been reported the formation of this product. The concentration of *m/z* 215 was formed in the first 15 min. When the reaction progressed, the concentration of P1 was remained stable in 15-45 min, and then decreased in 60 min. The other important intermediate P2 was *m/z* 124, corresponding to 2-amino-4,6-dimethylpyrimidine. The formation of P2 was formed by sulfonamide bond cleavage since the sulfonamide antibiotics can oxidized by reactive oxygen species. The concentration of P2 was produced rapidly, but they keep constant in a low level with the time prolonging. The proposed SMZ degradation products were presented in Table S3.

Previous studies indicated that the solution pH could influence the generation of oxidative species in the photodegradation process. Fig. S5 indicated that the degradation rates of SMZ were increased with the augmentation of initial pH. At low pH conditions, $\bullet O_2^-$ may prefer to combine with H^+ to form H_2O_2, which inhibits the degradation of SMZ [72]. Fig. S6a showed that the SMZ degradation rate by PCN-DP-0.2 was slightly dropped from 0.087 min^{-1} to 0.078 min^{-1} after four cycles. This decrease of degradation efficiency may attribute to the degradation products covering the active sites of catalyst. In addition, after cycle photocatalytic reactions, the used PCN-DP-0.2 sample was further characterized by XRD, TEM and XPS. As shown in Fig. S6b-f, no noticeable changes in the crystal, morphology, and surface structure are found, which suggests the high stability of pyrazine modified photocatalyst in the SMZ degradation system.

This modification strategy was also enhances the photocatalytic H_2 evolution activity since more photoelectrons are available over pyrazine doping PCN [73]. As shown in Fig. 5a, all samples are active for H_2 evolution with visible light illumination. The optimized sample (PCN-DP-0.2) exhibited best photocatalytic efficiency among all photocatalysts studied. The average H_2 evolution rate of PCN-

DP-0.2 reaching up to 63 μmol h^{-1}, is almost 6.3 times in comparison with that of pristine PCN (10 μmol h^{-1}). When excessive pyrazine was doped, an adverse effect about H_2 evolution was emerged due to the excessive foreign units may destruct the conjugated framework. The stability of PCN-DP-0.2 was evaluated for a long-term photocatalytic reaction (Fig. 5b), in which slight decrease of photocatalytic activity was observed after four cycles, indicating PCN-DP-0.2 possessed excellent stability. The TEM image of PCN-Pt and PCN-DP-0.2-Pt was presented in Fig. 5c and Fig. 5d-e, respectively, which indicated that the Pt particles of small size are much more evenly dispersed on the surface of PCN-DP-0.2 sample. Furthermore, the results of XPS and TEM image for the fresh and used PCN-DP-0.2 indicated that the as-prepared sample are chemically stable (Fig. S7). These above results indicated that our strategy was simple and the as-prepared photocatalysts have higher photocatalytic activity [74, 75].

3.3 Mechanism of the enhanced photocatalytic activity

Carbon materials have excellent electrical conductivity. So, we think that pyrazine in the structure of PCN can act an electron channel and quicker transfer the electrons than the original layer. The efficient separation of electron-hole pairs was further demonstrated by photocurrent measurements and electrochemical impedance spectroscopy (EIS) [76]. Fig. 6a showed that both samples exhibited stable photocurrents during the light on and off cycles. Among these samples, the photocurrent of PCN-DP-0.2 was 3 times higher than that of the PCN, suggesting that more efficient separation of photogenerated charge carriers was achieved. Meanwhile, compared with PCN, all the modified samples showed a smaller semicircular Nyquist plots diameter (Fig. 6b), suggesting a charge transfer resistance, and leading to more efficient separation of photogenerated charge carriers. It can be seen that the DP doping is beneficial for the separation and transfer of photogenerated carriers.

The separation rates of charge carriers in carbon nitride were investigated by photo-luminescence (PL) test. As shown in Fig. 7a, the peak at 460 nm of PCN was assigned to the band-to-band layer recombination of photogenerated carriers. Remarkable PL quenching of this peak was obtained in PCN-DP samples (from 460 nm to 470 nm), indicating the recombination of charge carriers was restricted in PCN-DP samples. Moreover, the pyrazine can be acted as a hyperchannel to transfer the photogenerated electrons, which was beneficial for electron-holes separation. Time-resolved fluorescence decay spectroscopy (TRPL) was further to demonstrate it. Fig. 7b and Table S4 suggested the lifetime of PCN-DP-0.2 (5.64 ns) was shorter than that of the PCN (8.34 ns). This decreased lifetime indicated that the exciton dissociation was improved by pyrazine doping [77]. PL quenching was further examined by the photographs of PCN and PCN-DP-0.2 powders or their suspensions in water with UV light illumination. As shown in Fig. 7c, compared with the PCN, the PCN-DP-0.2 displayed much lower intensity of luminescence obviously in powder and suspensions, which was in consistent with the results of PL [54].

ESR measurements and trapping experiments were carried out to demonstrate photodegradation mechanism of SMZ by PCN and PCN-DP-0.2. As shown in Fig. 8a, no signal of DMPO-•O_2^- was detected in dark for both PCN and PCN-DP-0.2 samples. The signal of DMPO-•O_2^- (an intensity ratio of 1:1:1:1 signal) was increased with the increase of irradiation time. Moreover, the intensity signals of DMPO-•O_2^- for PCN-DP-0.2 was higher than PCN those of the PCN in 4 min and 8 min visible light irradiation, respectively. Meanwhile, the signal of DMPO-•OH (an intensity ratio of

1:2:2:1 signal) was obviously detected in the DMPO water solution for PCN-DP-0.2 (Fig. 8b). However, the signal of DMPO-•OH for PCN was too weak to be detected. Furthermore, trapping experiments by different scavengers (IPA for •OH, CAT for H_2O_2, TEMPOL for $•O_2^-$, and EDTA for h^+) were carried out. As shown in Fig. 8c and 8d, the addition of TEMPOL and EDTA inhibited 84.6% and 62.4% of SMZ degradation, respectively, indicating that the $•O_2^-$ and h^+ mainly accounted for the SMZ degradation. About 30% of SMZ degradation was suppressed in the presence of CAT, suggesting that H_2O_2 had a positive effect for photocatalytic degradation of SMZ. IPA showed no significant impact on the SMZ photodegradation. This result indicated that the main active species were $•O_2^-$ and h^+. Therefore, the main effect of pyrazine doping in PCN seems to accelerated the conduction band (CB) electron transfer to O_2 with generating more $•O_2^-$ and •OH for reaction.

Combining the above results, the possible pathways of PCN-DP for SMZ degradation (system I) and H_2 evolution (system II) were proposed in Scheme 1. Evidently, the electronic structure is largely modified by the incorporation of pyrazine molecules due to the doping can alter the thermal polymerization route. Pyrazine can act as electron-acceptor to separation the charge carrier combination of PCN-DP. Under visible light irradiation, the catalyst was excited, and then generated electrons and holes. In the system I, the photocatalytic degradation of SMZ by PCN-DP was attributed to reactive oxygen species (such as $•O_2^-$, H_2O_2 and •OH) and the interfacial interactions of contaminant with photocatalysts. The distorted structure and widen visible light absorption enhanced the migration efficiency of photogenerated electrons, causing a high yield of $•O_2^-$. In addition, the holes can directly decompose the pollutants. For the water splitting (system II), since the band structure of PCN-DP was modified, which make more photogenerated carriers generated from it. Pt particles are evenly dispersed on the surface of PCN-DP-0.2 sample due to the pyrazine channel. The synergistic effect of Pt and pyrazine channel induces the high activity of H_2 evolution for PCN-DP-0.2 sample.

3.4 Phytotoxicity measurements results

Seed germination and radicle elongation tests are usually used to assess the plant toxicity of contaminants and contaminated environment [78]. In this study, Chinese cabbage (Brassica rapa L.) was choose since its seed has the advantages of uniform size (1-2 mm), rapid germination and is sensitive to antibiotics. In the seed germination stage, Chinese cabbage seeds began to germinate after 8 h. As shown in Fig. 9a and Fig. S8, the germination percentage of control and treatments generally reached over 92% after 24 h of incubation, respectively. The results of the phytotoxicity experiments exhibited that sulfamethazine (SMZ) solution or photocatalyst had no universal effect on seed germination stage. This may be ascribed to seed coat on the embryo of seeds. In the radicle elongation stage, the seed radicle length in SMZ solution (mean length of 8.89 mm, n=80) was obviously lower than that the blank sample (mean length of 14.76 mm, n=80) (Fig. 9b and Fig. 9c). However, the degraded SMZ solution (after photocatalysis by PCN-DP) showed no inhibition on seed radicle length (mean length of 16.11 mm, n=80). In addition, the PCN and PCN-DP-0.2 samples showed no influence on radicle elongation. This result indicated that the toxicity of SMZ polluted water after degradation is greatly reduced, and the treated water is clean and environmentally friendly. Moreover, the as-prepared photocatalysts are environmentally friendly.

4. Conclusions

In summary, a highly efficient photocatalyst was prepared via a bottom-up method, which involves pyrazine doping, thermal-induced exfoliation and condensation/polymerization. Both morphology and electronic structures of pyrazine doped PCN were greatly modified via molecule doping of pyrazine. The electron-deficiency pyrazine can acted as a hyperchannel to transfer the photogenerated electrons, which was beneficial for electron-holes separation. As a result, an overall enhanced SMZ degradation rate and H_2 production rate of PCN-DP were achieved, which was consistent with the extended visible light absorption. The photocatalytic degradation of SMZ by PCN-DP was attributed to reactive oxygen species (such as $\bullet O_2^-$, H_2O_2 and $\bullet OH$) and the interfacial interactions of pollutant with photocatalysts. In addition, Phytotoxicity experiments were conducted, which shows that the toxicity of sulfamethazine after degradation is greatly reduced and the as-prepared photocatalyst is environmentally friendly. Although some achievements have been made, the problem of catalyst recovery is still involved, further optimization is needed.

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Figure captions:

Fig. 1. (a) Powder XRD patterns, (b-c) FT-IR spectra of PCN and PCN-DP-x samples; high-resolution XPS spectra of (d) survey, (e) C 1s and (f) N 1s for PCN and PCN-DP-0.2.

Fig. 2. SEM images of (a) PCN, (b) PCN-DP-0.1, (c) PCN-DP-0.2, and (d) PCN-DP-0.4. TEM images of (e) PCN and (f) PCN-DP-0.2.

Fig. 3. (a) Solid-state ^{13}C MAS NMR spectra, (b) EPR spectra of PCN and PCN-DP-0.2, (c) UV-vis diffraction reflectance spectra of PCN and PCN-DP samples and the Tauc plots of PCN and PCN-DP-0.2 (inset), (d, e) Mott–Schottky plots, and (f) Schematic band structure of PCN and PCN-DP-0.2.

Fig. 4. (a) Photocatalytic degradation of SMZ, (b) degradation rate of SMZ on PCN and PCN-DP-x samples, (c) LC spectrum of SMZ solution degraded by PCN-DP-0.2, and (d) Evolution of the product ions and decrease of SMZ in the photocatalytic degradation of SMZ over PCN-DP-0.2.

Fig. 5. (a) Photocatalytic H_2 evolution performance for PCN and PCN-DP-x samples, (b) cycle measurements of H_2 evolution of PCN-DP-0.2, (c) TEM image of Pt deposited PCN, (d) TEM image of Pt deposited PCN-DP-0.2 and (e) EDS of Pt deposited PCN-DP-0.2.

Fig. 6. (a) Photocurrent response curves and (b) EIS Nyquist plot of PCN and PCN-DP-x samples.

Fig. 7. (a) Room temperature steady state photoluminescence (PL) emission spectra, (b) time-resolved fluorescence decay spectra of PCN and PCN-DP-x sample with an

excitation wavelength of 365 nm, (c) Photographs of PCN and PCN-DP-0.2 powders and suspensions under 365 nm irradiation.

Fig.8. ESR signals of (a) DMPO-•O_2^- adducts in methanol dispersion and (b) DMPO-•OH adducts in methanol dispersion over PCN and PCN-DP-0.2, (c and d) reactive species trapping experiments of PCN-DP-0.2 under visible light irradiation.

Fig. 9. (a) Effect of SMZ solution and photocatalyst on seed germination for 24 h (n= 160), (b) Effect of SMZ solution and photocatalyst on Chinese cabbage seeds radicle length for another 24 h (n = 80). Boxes illustrate the first quartile, median and third quartile of the data. The mean is marked with a dotted line in the box. The ends of the whiskers represent the 5th percentile and the 95th percentile. Values beyond 1.5 times the box height are outliers plotted as circles. (c) Micrograph of seed radicle elongation stage.

Scheme 1. Possible pathway of PCN-DP for SMZ degradation (system I) and H_2 evolution (system II)

Table 1 Surface area and pore volume for PCN and PCN-DP samples.

Samples	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
PCN	82.87	0.45	2.73
PCN-DP-0.1	89.96	0.48	2.74
PCN-DP-0.2	76.45	0.36	3.94
PCN-DP-0.4	71.39	0.34	2.74