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Enhancement of photocatalytic hydrogen evolution activity of
porous oxygen doped g-C₃N₄ with nitrogen defects induced by
changing electron transition

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Abstract: Porous structure, nitrogen defects and oxygen dopants are simultaneously introduced into the framework of graphitic carbon nitride (g-C₃N₄) by a simple co-pyrolysis of dicyandiamide and ammonium persulphate ((NH₄)₂S₂O₈). The (NH₄)₂S₂O₈ plays multi-function roles in the co-pyrolysis process---It not only restrains polycondensation to generate nitrogen defects but also introduces porous structure and oxygen dopants due to its strong oxidative ability. The synergetic effect of the nitrogen defects and oxygen dopants leads to the change of π band state and LP state (lone pair electrons), causing the change of electron transition in the modified g-C₃N₄. The transitions from impurity levels play a predominant role in excitation process while the transition from intrinsic HOMO to LUMO becomes subordinate, which improve the charge separation significantly. The modified g-C₃N₄ exhibits excellent photocatalytic hydrogen evolution activity under visible light illumination, which is almost ~~six~~6 times higher than pristine g-C₃N₄ because of the improved efficiency of charge separation and increased specific surface area. These findings provide a simple and efficient method to improve the photocatalytic activity of g-C₃N₄ by changing the electron transition through a rational band structure engineering.

Key words: Photocatalytic hydrogen evolution, g-C₃N₄, nitrogen defects, oxygen doping, electron transition

1. Introduction

With the continuous development of the world and the increasing demand for clean and sustainable energy, hydrogen energy as a promising ideal alternative to fossil fuel

has been intensively attractive, especially hydrogen evolution from water splitting driven by sun light. Graphitic carbon nitride (g-C₃N₄), a new metal-free polymeric photocatalyst, has stimulated tremendous research attention for hydrogen evolution due to its excellent physiochemical property, such as high thermal and chemical stability, suitable electronic band structure, low-cost and easy preparation [1-6]. However, the photocatalytic performance of bulk g-C₃N₄ is still unsatisfactory due to its low electrical conductivity, limited optical absorption and fast photogenerated charge carrier recombination [7-10]. After years of effort, several strategies have been developed to improve the photocatalytic activity of g-C₃N₄, including the construction of a porous structure [11], element doping [12], modification with carbon material [13], noble metal deposition [14] and coupling with other semiconductors to form hybridized composites [15].

The porous structure provides readily accessible channels for reactant adsorption, and more surface-active sites for reaction [16]. The general method to construct porous structure for catalytic reactions, includes hard-templating and soft-templating methods [17, 18]. However, the method generally uses hazardous and environmentally unfriendly chemicals such as ammonium fluoride or hydrogen fluoride to remove the template, and also introduces carbon residue, which is undesirable for photocatalysis. Therefore, it is necessary to develop a simple method to construct structurally porous g-C₃N₄. In addition, it is widely used to introduce nitrogen defects into g-C₃N₄ framework for improving its photocatalytic activity. Niu et al [19]. reported that the introduction of nitrogen vacancy exerted remarkable effects on modifying the electron structure of g-C₃N₄. The intrinsic radiative recombination of charge carriers is greatly restrained. Thus, the nitrogen deficient g-C₃N₄ showed improved photocatalytic activity for hydrogen evolution and decomposition of Rhodamine B under both UV-visible and visible light. Zhang et al [20]. found that the photocatalytic hydrogen evolution rate of g-C₃N₄ with the introduction of two types of nitrogen defects (cyano group and nitrogen vacancy) is 26 times higher than that of bulk g-C₃N₄. It was mainly ascribed to the combination effect of porous feature, as-formed defects and increased specific surface area. Yu et al [21]. demonstrated that the band structure of g-C₃N₄ could be adjusted by cyano groups and surface nitrogen vacancies, which are favorable for harvesting visible light and separate photoexcited charge carriers efficiently.

Besides, nonmetal heteroatom (O, S and P) doping is also an effective method to alter the band structure, improve separate rate of charge carriers and expand the range of light absorption for g-C₃N₄ [22-24]. Therein, oxygen doping has attracted much attention due to its easy preparation and good performance. Li et al. [25] prepared oxygen-doped g-C₃N₄ for the first time by using a facile H₂O₂ hydrothermal approach which improved the surface area, extended the visible light response of g-C₃N₄, and enhanced the separation efficiency of photogenerated charge carriers. Huang et al. [26] fabricated a porous oxygen-doped g-C₃N₄ by a facile precursor pre-treatment method, which showed excellent photocatalytic H₂ evolution activity with apparent quantum efficiency of 7.8% at 420 nm. Additionally, Qiu et al. [27] developed a novel metal-free oxygen doped porous graphitic carbon nitride, which displayed a high

initial rate of hydrogen evolution ($0.098 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) due to the increase of specific surface area, the improvement of charge separation rate, and red-shift of light adsorption edge (up to 700 nm). However, to our best knowledge, the combination of nitrogen defects and nonmetal heteroatom doping in the porous g-C₃N₄ has rarely been reported.

The present work reports on a simple one-pot co-pyrolysis method that produces a porous oxygen doped g-C₃N₄ with nitrogen defects (modified g-C₃N₄), which presents 6 times improved photocatalytic activity compared to pristine g-C₃N₄. It is found that (NH₄)₂S₂O₈ plays multiple roles during the thermal polymerization process. More importantly, the path of electron transition has been changed by the introduction of nitrogen defects and oxygen dopants, which affects the π band state and LP state in the modified g-C₃N₄. Thus, the charge separation is improved significantly. The excellent photocatalytic activity of the modified g-C₃N₄ is ascribed to the increased surface area of porous structure, enhanced light absorption and improved charge separation. Our findings reveal the important role of ammonium persulfate to synthesize modified g-C₃N₄ and provide a different idea to improve the photocatalytic activity of g-C₃N₄ by changing electron transition, which is caused by the synergetic effect between nitrogen defects and oxygen dopants.

2. Experimental section

2.1 Materials and reagents

Dicyandiamide was purchased from Aladdin Industrial Corporation. (NH₄)₂S₂O₈ was supplied by Tianjin kaitong chemical reagent Co., Ltd, China. Triethanolamine (TEOA) was also provided by Aladdin Industrial Corporation. All reagents used in this study were at least in analytical grade without further purification. Deionized water was used for all experiments.

2.2 Preparation of photocatalysts

The porous g-C₃N₄ samples were synthesized by a one-step pyrolysis treatment of dicyandiamide and a certain amount of ammonium persulphate. The simple preparation method is as follows: dicyandiamide (2 g) and a certain amount of ammonium persulphate were uniformly mixed and ground thoroughly. Then the powders were put into muffle furnace and heated at 550 °C for 4 h with a heating rate of 5 °C/min. When the program was finished, the furnace was cooled to room temperature automatically. The samples with mass ratios of ammonium persulphate to dicyandiamide of 0.25:1, 0.5:1, and 0.75:1 were signed as p-CN1, p-CN2, and p-CN3, respectively. For comparison, a bulk g-C₃N₄ sample was prepared by the pyrolysis of dicyandiamide without adding ammonium persulphate. Following the synthesis, all products were collected, grounded and washed repeatedly with deionized water, and then dried at 60 °C for 10 h.

2.3 Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 45 kV and 200 mA, respectively. Data were recorded at a scan rate of $0.02^\circ 2\theta \text{ s}^{-1}$ in the 2θ range from 5° to 55° . Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 spectrometer, and the samples were prepared as KBr pellets. X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo ESCALAB250 instrument with a monochromatized Al K α line source (200 W). Nitrogen adsorption–desorption isotherms were collected at a Micromeritics ASAP 2020 surface area and porosity analyzer. The sample was degassed at 413 K for 5 h and then analyzed at 77 K. The relative pressure (P/P_0) range used for calculation of BET surface area was from 0.05 to 0.35. The scanning emission microscope (SEM) measurements were conducted using a FEI Nova Nano SEM 230 Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) image was recorded using a JEOL Model JEM 2010 EX instrument at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were performed on a UV-Vis spectrophotometer (Lambda 900, PerkinElmer, USA). BaSO₄ was used as a reflectance standard. The optical properties were evaluated by $F(R)$, and they were applied with a Kubelka-Munk correction. Photoluminescence spectra were recorded on a LabRAM HR spectrometer (HORIBA Jobin Yvon, France) under the excitation wavelength of 325 nm at room temperature. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3510.00 G; microwave frequency, 9.79 GHz; power, 5.05 mW.

2.4 Photocatalytic H₂ evolution

Photocatalytic H₂ production experiments were performed in a 150 mL quartz reactor at ambient temperature and atmospheric pressure. A 300 W Xe lamp coupled with a UV cut-off filter ($\lambda > 420 \text{ nm}$) was used as the light source. In a typical experiment, 50 mg of photocatalyst powder was suspended in 50 mL of an aqueous triethanolamine solution (20 vol%). Surface functionalization of the g-C₃N₄ photocatalysts with Pt cocatalyst (nominal loading 3 wt%) was achieved by directly dissolving an appropriate amount of H₂PtCl₆ into the aqueous triethanolamine solution (20 vol%), followed by illumination with the 300 W Xe lamp for 60 min at room temperature. For the H₂ production tests, dispersions of Pt/g-C₃N₄ in aqueous triethanolamine solution (20 vol%) were sonicated to achieve good dispersion and deaerated by bubbling N₂ through the reaction mixture for 30 min. The reactor was then irradiated by the 300 W Xe lamp coupled with a UV cut-off filter ($\lambda > 420 \text{ nm}$), and H₂ evolution was monitored by an online photocatalytic reaction system (CEL-SPH2N, CEAULIGHT, Beijing). At 1 h time intervals, the hydrogen evolved was quantified by a gas chromatograph (GC D7860, TCD detector, N₂ carrier, 5A molecular sieve column, Shanghai Jinghe Chromatograph Co., Ltd). Moreover, by using the similar procedure as above, 50 mg of photocatalyst was used for the apparent quantum yield (AQY) measurement under the wavelengths of 420, 450, 500

and 600 nm band-pass filters, respectively. The AQY was calculated by the following equation:

$$\text{AQY (\%)} = 2 \times \text{number of evolved H}_2 \text{ molecules} \times 100 / \text{number of incident photons}$$

2.5 Photoelectrochemical measurements

Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode, the active area is confined to 0.25 cm². The electrolyte was 0.1 M Na₂SO₄ aqueous solution without additive (pH 6.9). The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of solution containing 980 μ L absolute ethanol of and 20 μ L of Nafion solution, and the mixed solution was under ultrasonication for 30 min to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the working electrode was further dried at 373 K for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The transient photocurrent was obtained by using a 30 s on-off light cycle at a bias voltage of 0.2 V. Electrochemical impedance spectra were collected in the frequency range from 0.01-10⁶ Hz with a 5 mV sinusoidal AC voltage. The Mott-Schottky plots were measured at the frequency of 1000 Hz. The visible light source came from a 300 W Xe lamp with a filter ($\lambda > 420$ nm).

3. Result and discussion

3.1. Structural properties of as-prepared samples

Fig. 1a shows the synthesis process of modified g-C₃N₄. The detailed synthesis procedure is described in experimental section. The morphologies of bulk g-C₃N₄ and p-CN2 were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. S1 and Fig. 1b-e. From the SEM images in Fig. S1A, dense and thick layers could be observed in g-C₃N₄, which would suppress its capabilities of light absorption, charge and mass transport [28]. After (NH₄)₂S₂O₈ treatment, the p-CN2 exhibits a loose and porous morphology, as shown in Fig. S1B. In Fig. 1b and 1d, it is clearly that large sized and overlapped nanosheets can be seen in the TEM image for bulk g-C₃N₄. After the modification of (NH₄)₂S₂O₈, the size of nanosheets is reduced and some pores are clearly presented in p-CN2 (Fig. 1e, marked by blue dash circle). Compared with g-C₃N₄, p-CN2 appears the contrast of TEM image of in p-CN2 is much brighter in the TEM image, indicating that its thickness is thinner.

As shown in Fig. 2a, a similar crystalline structure is detected for both bulk g-C₃N₄

and p-CN2. The main diffraction peaks are observed at around 13.0° and 27.5° , corresponding to the in-planar structurally repeated motifs of triazine rings and the interlayer reflection of the graphitic structure, respectively [29, 30]. Compared to that of g-C₃N₄, the peak of p-CN2 shifts slightly from 27.5° to 27.3° and the intensity becomes weaker. It indicates that the interlayer stacking distance of p-CN2 is increased, which is in accordance with the TEM result. In addition, the Fourier transform infrared (FTIR) spectroscopy (Fig. 2b) is further used to confirm that the typical molecular skeletal vibration modes in p-CN samples are close to those in g-C₃N₄. The extra peak at 2180 cm^{-1} is obviously observed in the p-CN samples. It is assigned to C $\equiv$ N triple bonds, indicating the existence of cyano groups (C $\equiv$ N) in p-CN2 [31]. It may be ascribed to the suppression of polycondensation after the addition of (NH₄)₂S₂O₈. As we know, dicyandiamide is polymerized into melamine at 234°C [6, 32] while (NH₄)₂S₂O₈ is decomposed to NH₃ (g), SO₂ (g) and O₂ (g) at 120°C , which would act as a role in separating some dicyandiamide crystal grains and dicyandiamide derived intermediates in space and suppressing the formation of integrated tri-s-triazine structure at 550°C . The sharp peak about 808 cm^{-1} is assigned to typical breathing mode of the triazine units. However, the strong bands in the region from 900 to 1800 cm^{-1} are typical for the melon containing C–N–C heterocycles and are generally associated with skeletal stretching vibrations of aromatic rings, the peaks at 2900 – 3600 cm^{-1} can be assigned to adsorbed water or amine groups [33].

It can also be seen from Fig. 2c and 2d that all the samples exhibit type IV isotherms with H3 hysteresis loops, which demonstrates the presence of mesoporous structure [34]. For (NH₄)₂S₂O₈ modified g-C₃N₄ samples, the hysteresis loops shift to the region of lower relative pressure and the areas of the hysteresis loops become enlarged, **indicating the increase of mesoporosity increases—compared with bulk g-C₃N₄.** As shown in Table S1, the surface area is increased progressively from $11.7\text{ m}^2\text{ g}^{-1}$ to $36.9\text{ m}^2\text{ g}^{-1}$ with the increased mass of (NH₄)₂S₂O₈, which is ascribed to the possible space-occupying effect of undecomposed (NH₄)₂S₂O₈. However, when the mass of (NH₄)₂S₂O₈ is increased to 0.75 g , the BET surface area and pore volume of the sample (p-CN3) are sharply decreased. This is because the excess undecomposed (NH₄)₂S₂O₈ may occupy the generated pores thus decrease the surface area (ca. $19.75\text{ m}^2\text{ g}^{-1}$). The change of morphology could also be observed in the TEM images (Fig. S2B). In addition, the wide distributions of BJH pore size in the range of 20 – 100 nm further confirm the formation of different sized pores. Therefore, the (NH₄)₂S₂O₈ plays an important role in facilitating the formation of porous structure during the polycondensation process.

The XPS measurements were carried out to determine the chemical states of the elements for bulk g-C₃N₄ and p-CN2. Signals of C, N and O elements are displayed in the spectra survey for the two samples (Fig. 3a). As expected, the C1s spectra in Fig. 3b show three main peaks, which could be assigned to adventitious carbon species (284.6 eV), C–NH_x ($x = 1, 2$) on the edges of heptazine units (286.2 eV) and N–C=N coordination in the framework of g-C₃N₄ (288.0 eV), respectively [21]. Meanwhile, as

shown in Fig. 3c, the N 1s XPS spectra for the samples contain three components at 398.7, 400.1, and 401.1 eV, corresponding to sp^2 bonded N in the tri-s-triazine (N_{2C}), bridging nitrogen atoms in $N-(C)_3$ and NH_x groups in the heptazine framework, respectively. Additionally, the very weak peak at 404.2 eV was attributed to the charging effects or positive charge localization in the heterocycles [35]. The O 1s spectra of the two samples were fitted into two peaks at 533.1 and 531.8 eV, which were ascribed to the adsorbed water and CO_2 , respectively [25, 36]. In comparison with the $g-C_3N_4$, the binding energies of C 1s, N 1s and O 1s spectra in p-CN2 show a little bit of variations. In C 1s spectrum, the intensity of the peak located at 284.6 eV increases, indicating the loss of lattice nitrogen and the formation of nitrogen vacancy in p-CN2 [16], and the peak at 286.2 eV is more intensified compared to the same feature for $g-C_3N_4$ (Fig. 3b, bottom), which can be taken as additional evidence for the **existence** of cyano groups (as seen by FTIR) since $C\equiv N$ groups possess similar C 1s binding energies to $C-NH_x$ [37]. Surprisingly, a new peak at 288.7 eV is observed in p-CN2, which may be attributed to the C atoms bonded with O (C-O) [26, 38]. In the N 1s spectrum, the N_{3C} and N_{2C} peaks in p-CN2 exhibit a small shift to lower binding energy, which could be ascribed to the **existence** of cyano groups whose N 1s binding energy are intermediate between those of N_{2C} and N_{3C} . Furthermore, the ratio of $N-sp^2/N-sp^3$ increases from 1.91 for pristine $g-C_3N_4$ to 3.71 for p-CN2 in Table S2, implying the **existence** of cyano groups on the N_{2C} lattice sites in p-CN2. To further confirm the introduction of surface N defects, the element contents in the two samples are further compared by elemental analysis (Fig. S3). The atomic ratios of carbon to nitrogen agree almost 0.66 for bulk $g-C_3N_4$, lower than 0.70 for the p-CN2, while the surface atomic ratio from XPS reveals that the C/N molar ratio of pristine $g-C_3N_4$ (0.85) is also lower than that of p-CN2 (0.89) (Table S3), indicating the nitrogen vacancy exists in the p-CN2 nanosheets. For O 1s spectrum, a new peak at the low binding energy of 530.7eV appears in p-CN2 sample, which may be assigned to C–O and N–C–O species in lattices [39]. Although both the C 1s peak and O 1s peak demonstrate that C-O bond may be generated in p-CN2, it still needs to be confirmed further. Besides, no signals belonging to sulfur species can be found in p-CN2 (Fig. S4), indicating that the sulfur atom may be released as gaseous form and has not been incorporated into the lattice of $g-C_3N_4$ during heating treatment.

To confirm the existence of the nitrogen defects and oxygen dopants in p-CN2 sample, room-temperature electron paramagnetic resonance (EPR) spectra were recorded. In Fig. 3e both bulk $g-C_3N_4$ and p-CN2 exhibit a paramagnetic absorption signal with the g value of 2.0034, which can be assigned to the unpaired electrons on sp^2 -carbon atoms within the π -conjugated aromatic rings. Compared with that in bulk $g-C_3N_4$, this EPR signal in p-CN2 is much declined, which can be ascribed to the substitution of O to N forming covalent bonds with C, reducing the number of unpaired electrons and decreasing the EPR signal. In addition, the shoulder peak appears at $g=1.9884$, probably because of the substitution of the N atom in the heptazine unit with an O atom creates one unpaired spin [38]. The g value is different from that in the reference, and it may be ascribed to the different substitution sites of

nitrogen atoms. On the basis of the characterization results, the possible chemical structure of p-CN2 is proposed in Fig. 3f.

3.2. Optical and electronic properties of the photocatalysts

To investigate the band structure and photo absorption ability, the UV-vis DRS spectra were carried out and showed in the Fig. 4a. It is obvious to see that the absorption edges in p-CN2 show a remarkable blue-shift in comparison with the bulk g-C₃N₄, which is consistent with the color variation from yellow bulk g-C₃N₄ to light yellow p-CN2 (insets in Fig. 4a). The bandgap energies of all samples are derived by Kubelka-Munk method [12]. Fig. 4b shows the bandgap of p-CN2 (2.75 eV) is a little larger than that of g-C₃N₄ (2.7 eV), which may be ascribed to the quantum confinement effect (QCE) induced by the decline in thickness of p-CN2. In addition, an optical absorption tail could be found in p-CN2, hinting that defect state or dopant level may be generated. Thus, new generated energy levels are also derived from UV-vis spectrum of p-CN2, known as defect states. From valence band (VB) XPS spectra, the positions of VB maxima are estimated to be 2.1 eV and 1.94 eV for pristine g-C₃N₄ and p-CN2, respectively (Fig. S6). The diagram of band structure will be shown later.

As shown in Fig. 4c, when the samples were excited by 380 nm laser, a broad PL emission peak at ca. 470 nm appeared. An obvious red-shift of the emission peak from 480 to 508 nm can be found for bulk g-C₃N₄ to p-CN2, which may contradict to the UV analysis. In fact, it confirms the formation of defect states. Besides, the shape of emission peak is changed obviously, suggesting that the electron transition path is also changed. As we know, the electronic band states of g-C₃N₄ are composed of the δ band (sp^3 C-N bonding), π band (sp^2 C-N bonding), and lone pair (LP) state of the bridge nitride atom. In order to figure out the band structure and electron transition, the PL spectrum of p-CN2 is fitted by three Gaussian peaks, which are exhibited at 440-460 nm (peak A), 490-510 nm (peak B), and 530-560 nm (peak C), as shown in Fig. 4d. The luminescence emission peak A reflects the intrinsic radiative emission of the charge transition from the highest occupied molecular orbital (HOMO) which comprises 2p orbitals of low coordinated N atoms, to the lowest unoccupied molecular orbital (LUMO), which mainly consists of the C 2p character. The intensity of peak A drops sharply after modification of (NH₄)₂S₂O₈, suggesting the intrinsic radiative recombination is suppressed. The emission peaks B and C correspond to the transitions between antibonding π^* -LP and antibonding π^* - π , respectively. The ratios of these two peaks increase in p-CN2, suggesting that the corresponding electron transitions become predominant [40]. It may be ascribed to the increased amount of sp^2 C-N bonding, which is induced by the formation of nitrogen vacancy. In addition, oxygen atom preferentially occupies the site of bridge nitrogen atom, therefore the LP state is also affected. Thus, nitrogen vacancy and oxygen dopant have effects on the band structure of g-C₃N₄ because of the variation on the number of sp^2 C-N bonds and bridge nitrogen atoms, leading to the change of electron transition and suppression of charge recombination.

Photoelectrochemical measurements including transient photocurrent under visible light and electrochemical impedance spectra (EIS) irradiation were performed to further study the **separation and transportation of photogenerated carriers**. It could be seen in Fig. 5a that both pristine g-C₃N₄ and p-CN2 electrodes show obvious positive photocurrents by several on-off cycles of visible-light irradiation at an applied potential of -0.2V (vs. Ag/AgCl, pH 6.9) [41]. Additionally, p-CN2 shows larger photocurrent density than the bulk g-C₃N₄ electrode, indicating that the charge separation in p-CN2 is more efficient than that in pristine g-C₃N₄. Besides, it is obvious in Fig. 5b that the diameter of the semicircular Nyquist curve of p-CN2 is smaller than that of bulk g-C₃N₄, implying that the resistance at the solid/electrolyte interface is significantly decreased. It is benefit to charge transfer, which also suggests that the efficiency of charge separation is much higher in p-CN2.

3.3. Photocatalytic performance

The photocatalytic performance of bulk g-C₃N₄ and p-CN samples was evaluated by a typical time course of hydrogen production under visible light irradiation ($\lambda > 420$ nm) with 3 wt% Pt as co-catalyst at room temperature. As presented in Fig. 5c, all the p-CN samples show largely enhanced H₂ evolution activity. The H₂ evolution rate for both p-CN1(122.84 $\mu\text{mol h}^{-1} \text{g}^{-1}$) and p-CN3 (258.18 $\mu\text{mol h}^{-1} \text{g}^{-1}$) are higher than that of the bulk g-C₃N₄ (69.25 $\mu\text{mol h}^{-1} \text{g}^{-1}$). Among all the p-CN samples, p-CN2 displays the best photocatalytic performance with the H₂ evolution rate reaching 395.96 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which is approximately 6 times higher than that of bulk g-C₃N₄ (Fig. 5d). The results directly certify the positive effects of the (NH₄)₂S₂O₈ on promoting the photocatalytic activity of g-C₃N₄. **To explore the details of visible light driven activity for hydrogen evolution, the apparent quantum yield (AQY) was estimated at different wavelengths, as shown in Fig. S7. The AQY for p-CN2 was calculated to be 0.79% at $\lambda=420$ nm (Fig. S7), and the p-CN2 showed consistently higher AQY than pristine g-C₃N₄ at all wavelengths above 420 nm. In comparison, the g-C₃N₄ only showed activity at irradiation wavelengths below 450 nm, implying that more photons in p-CN2 can attend hydrogen evolution reaction. Besides, the stability test in Fig. S8 shows the photocatalytic H₂ production activity of p-CN2 is well retained ~~mained~~ after four successive cycles while the phase structures are not changed (Fig. S9), suggesting the high stability and durability of the catalyst.**

Based on the above characterization, the band structure is illustrated in Fig. S10. **Combined with the bandgap from UV-vis DRS, the CB edges of bulk g-C₃N₄ and p-CN2 are estimated to be -0.6 eV and -0.81 eV, respectively (Fig. 6). In addition, the upshift of CB edge in p-CN2 is also evidenced by using Mott-Schottky plots (Fig. S11). Obviously, the potential of conduction band in p-CN2 is more negative than that of g-C₃N₄, implying that p-CN2 possesses stronger photocatalytic reductive ability [42]. As mentioned above, the higher specific surface area of p-CN2 sample with porous structure is favorable for ~~to exposing~~ **more active sites to adsorb H⁺ and promoting mass transfer**. The bandgap of p-CN2 is a little larger than that of pristine g-C₃N₄, which is confirmed by UV-Vis DRS. However, the nitrogen defects and**

oxygen dopants introduce intraband states into the band gap of p-CN2, resulting in a lower excitation energy of excitons and a shorter migration path of the photo-generated electrons. The transitions from different impurity levels suppress the recombination of charge carriers. Thus, the porous oxygen doped g-C₃N₄ with nitrogen defects shows excellent photocatalytic hydrogen evolution activity, which is mainly ascribed to the synergetic effect between the nitrogen defects and oxygen dopants that promotes charge separation, and the increased surface area that provides more reaction sites for hydrogen production.

4. Conclusions

In summary, nitrogen defects and oxygen dopants have been successfully introduced into thin and porous g-C₃N₄ nanosheets by a facile method via polymerizing dicyandiamide and (NH₄)₂S₂O₈. Compared with bulk g-C₃N₄, the modified sample (p-CN2) exhibits an excellent photocatalytic hydrogen evolution activity with the rate up to 395.96 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which is almost ~~six~~6 times higher than that of pristine g-C₃N₄. The enhancement of photocatalytic activity is attributed to the increase in surface area and improved charge separation, which is induced by the synergetic effect between the nitrogen defects and oxygen dopants. The introduction of nitrogen defects and oxygen dopant leads to the change of π band state and LP state, which gives rise to the change of electron transition. Because the transitions from impurity levels play a predominant role in excitation process, the charge recombination is thus suppressed. In addition, it is found that (NH₄)₂S₂O₈ plays multi-function roles in the co-pyrolysis process. It not only restrains polycondensation to generate nitrogen defects but also introduces porous structure and oxygen dopants due to its strong oxidative ability. Thus, this work provides a different method to design highly efficient photocatalysts by affecting electron transition. It is worth noting that the present work can deepen our understanding on the complex excitation process in photocatalytic reaction and inspire us to improve the activity further by changing the band state of g-C₃N₄.

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Figure captions

Fig. 1. Schematic illustration for the formation of porous g-C₃N₄ (a).

TEM images of bulk g-C₃N₄ (b, d) and p-CN2 (c, e) samples.

Fig. 2. XRD patterns (a) and FTIR spectra (b) of bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples. Nitrogen adsorption-desorption isotherms (c) and pore size distribution (d) of bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples.

Fig. 3. XPS survey spectra (a), High-resolution C 1s spectra (b), N 1s spectra (c) and O 1s spectra (d) of bulk g-C₃N₄ and p-CN2 samples. Room-temperature EPR spectra for bulk g-C₃N₄ and p-CN2 samples (e), and the diagram of N-defected and O-doped tri-s-triazine unit in p-CN2 (f).

Fig. 4. UV-vis DRS spectra (a) and the bandgaps (b) of bulk g-C₃N₄ and p-CN2 samples, PL spectra (excitation wavelength: 380 nm) of bulk g-C₃N₄ and p-CN2 samples (c), and PL spectra deconvoluted into three Gaussian peaks at approximately (A) 450.9, (B) 494, and (C) 533.7 nm for p-CN2 (d). Inset of (d) shows the photoluminescence emission peaks A, B, and C, which indicate the electron transition from δ^* to LP, π^* to LP, and π^* to π states in a PL system, respectively

Fig. 5. Transient photocurrent responses under visible light of bulk g-C₃N₄ and p-CN2 samples. (a). Electrochemical impedance spectra of bulk g-C₃N₄ and p-CN2 samples (b). Photocatalytic H₂ evolution curves (c), and H₂ evolution rates (d) over bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3

samples.

Fig. 6. Possible mechanism for the photocatalytic H₂ production in bulk g-C₃N₄ and p-CN2, respectively.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Enhancement of photocatalytic hydrogen evolution activity of
porous oxygen doped g-C₃N₄ with nitrogen defects induced by
changing electron transition

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Fig. S1. SEM of bulk g-C₃N₄ (A) and p-CN₂ (B) samples

Fig. S1 displays the SEM images of bulk g-C₃N₄ (A) and p-CN₂ (B) samples. From the images, it is clear to see that the dense and thick layered structure exists in bulk g-C₃N₄ while loose and porous structure is shown in p-CN₂ sample.

Fig. S2. TEM images of (A, C) p-CN1, (B, D) p-CN3 samples.

In From the TEM images, it is clearly observed that the morphology of g-C₃N₄ varies
~~varied with the addition of (NH₄)₂S₂O₈ is clearly observed.~~ It is not benefit ~~to~~for the
 formation of porous structure during pyrolysis process when the addition of
 (NH₄)₂S₂O₈ is too low or ~~and~~ too much.

Fig. S3. C/N atomic ratio of bulk g-C₃N₄ and p-CN2 samples.

As show in Fig.S3, the C/N atomic ratio in p-CN2 is almost 0.71, higher than that in bulk g-C₃N₄ (0.66), hinting that surface nitrogen defects may be generated during the pyrolysis process.

Fig. S4. High-resolution XPS spectra of S₂p for bulk g-C₃N₄ and p-CN₂ samples.

The high resolution XPS spectrum for sulfur element has also been carried out. There are no signals of sulfur species appear in p-CN₂ sample, suggesting that sulfur atoms do not incorporate into the lattice of g-C₃N₄ during the pyrolysis process.

Fig. S5. UV-vis DRS spectra (a) of g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples, the bandgaps of (b) p-CN1 and (c) p-CN3 samples, PL spectra (d) (excitation wavelength: 380 nm) of bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples.

Fig. S5a shows the UV-vis DRS spectra of bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples. From the picture we can see that all samples showed the typical semiconductor adsorption. The absorption edges of p-CN1 and p-CN3 show a gradual blue-shift to longer wavelength in comparison with the bulk g-C₃N₄. Fig. S5b and Fig. S5c shows the optical bandgaps of p-CN1 and p-CN3 samples are 2.65 and 2.67 eV, respectively. The decrease of the band gap was contributed to the capturing of more visible photons, and potentially benefited for improving the photocatalytic performance, e.g., photocatalytic water splitting for hydrogen evolution. As shown in Fig. S6d, when the samples were excited by 380 nm visible light, a broad emission peak at ca. 480 nm appeared. An obvious red-shift of the emission peak from 485 to 508 nm was observed for the samples. Among the samples, the p-CN2 sample displays the lowest intensity, indicating that it possesses the lowest recombination rate

of holes and electrons.

Fig. S6. VB-XPS spectra and electronic band structures (b) of bulk g-C₃N₄ and p-CN2 samples

The valence band (VB) positions of both bulk g-C₃N₄ and p-CN2 were determined by the XPS valence spectra. As demonstrated in Fig. S6, the valence band of p-CN2 shows a negative shift compared with that of bulk g-C₃N₄.

Fig. S7. DRS spectrum of p-CN2 and wavelength dependent AQY of bulk g-C₃N₄ and p-CN2.

The wavelength dependency of apparent quantum yield (AQY) shows that the photoactivity of p-CN2 is directly related to its optical absorption spectrum, signifying that the photo-induced electron in the g-C₃N₄ polymer is the predominant driving force behind hydrogen production (Fig. S7). This result confirmed that the H₂ evolution is ~~was due exclusively due to~~ by the photocatalytic activity of p-CN2. In addition, the AQY of p-CN2 is higher than that of bulk g-C₃N₄ under the irradiation of all wavelengths. However, the optical absorption of p-CN2 is not as well as that of bulk g-C₃N₄ from UV-vis DRS, which suggests that more photons can be used by p-CN2 sample.

Fig. S8. Cycling stability test of p-CN2.

The operational stability of p-CN2 was tested by carrying out four cycles of photocatalytic H₂ production tests under identical experimental conditions and no significant change in the H₂ production activity was observed over the 4 test cycles.

Fig. S9. XRD patterns of the used bulk $\text{g-C}_3\text{N}_4$, p-CN1, p-CN2 and p-CN3 samples.

Based on the XRD characterization, no substantial changes in the phase and chemical structure of the samples were observed after four successive cycles (Figs. S9), confirming high stability and durability of the photocatalyst.

Fig. S10. VB-XPS spectra and electronic band structures of bulk g-C₃N₄ and p-CN2 samples

As presented in Fig. S10, combined with the bandgap values, the CB edges of bulk g-C₃N₄ and p-CN2 were estimated to be at -0.6_V and -0.81 V, respectively. The N deficiency and oxygen doping can introducing an intraband states into the band gap of p-CN2, resulting in a shorter migration path of the photo-generated electrons.

Fig. S11. Mott–Schottky plots for bulk g-C₃N₄ and p-CN2 samples.

The Mott-Schottky plots of bulk g-C₃N₄ and p-CN2 film electrodes ~~is were showned~~ in Fig. S11. The flat potentials of g-C₃N₄ and p-CN2 were calculated to be -1.21 V and -1.34 V , respectively. Therefore, the flat band potential shows a little negative-shift in p-CN2.

Table S1. BET and BJH pore volume of bulk g-C₃N₄, p-CN1, p-CN2 and p-CN3 samples.

Photocatalyst	Surface Area (m ² /g)	Average pore (cm ³ /g)
g-C ₃ N ₄	10.7	0.074
p-CN1	11.7	0.089
p-CN2	36.9	0.263
p-CN3	19.75	0.138

Table S2. The ratio between N_{sp^2}/N_{sp^3} in the obtained samples

Samples	g-C₃N₄	p-CN2
N_{sp^2}/N_{sp^3}	1.91	3.71

Table S3. Elemental analysis of g-C₃N₄ and p-CN2.

Samples	Cwt. %	N wt. %	Hwt. %	Owt. %	C/N
g-C ₃ N ₄	34.71	61.09	1.75	2.45	0.66
p-CN2	34.39	57.71	1.94	5.96	0.70

Table S4. Comparison of HER of p-CN2 and other metal-free g-C₃N₄ photocatalysts reported recently in the literature.

Samples	Light source	Catalyst use/cocatalyst loading	Reactant solution	Hydrogen evolution/ $\mu\text{mol h}^{-1} \text{g}^{-1}$	reference
p-CN2	300W Xe Lamp ($\lambda > 420 \text{ nm}$)	50 mg/3 wt% Pt	40 mL water+10 mL TEOA	395.96	This work
ONLH-600	300W Xe Lamp ($\lambda >$	30 mg/5 wt% Pt	45 ml water+5 mL TEOA	337	S1

	420 nm)				
Nitrogen-deficient g-C ₃ N ₄ .	300W Xe Lamp ($\lambda >$ 420 nm)	200 mg/3 wt% Pt	270 mL water+30 mL TEOA	123	S2
CN-0.1	300W Xe Lamp ($\lambda >$ 420 nm)	30 mg/3 wt% Pt	90 ml water+10 mL TEOA	277	S3
Pt/C ₃ N ₄ NTs	300W Xe Lamp ($\lambda >$ 420 nm)	100mg/3wt% Pt	90 ml water+10 mL TEOA	135	S4
CNS10	300W Xe Lamp ($\lambda >$ 400 nm)	100 mg/3 wt% Pt	90 mLwater+3 0 mLmethano l	121.6	S5
ACN	300W Xe Lamp ($\lambda >$ 440 nm)	50 mg/6 wt% Pt	270 mL water+30 mL TEOA	157.9	S6
O-doped g-C ₃ N ₄	300W Xe Lamp ($\lambda >$ 420 nm)	100mg/1.2 wt% Pt	90ml water+10 mL TEOA	375	S7
CNF	300W Xe Lamp ($\lambda >$ 420 nm)	100mg/3wt% Pt	90ml water+10 mL TEOA	130	S8

CNIC	300W Xe lamp ($\lambda >$ 420 nm)	100mg/3wt% Pt	90ml water+10 mL TEOA	50.2	S9
Au/g- C ₃ N ₄ - DP	500W HBO lamp with a water filter ($\lambda >$ 420 nm)	100mg/ an appropriate amount of H ₂ PtCl ₆	90ml water+10 mL TEOA	107	S10

Reference

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