N-doped graphitic carbon-incorporated g-C3N4 for remarkably enhanced photocatalytic H2 evolution under visible light

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Described herein is a facile one-pot strategy to synthesize N-doped graphitic carbon-incorporated g-C3N4 by adding slight amount of citric acid into urea as the precursor during thermal polymerization. The obtained materials retained the original framework of g-C3N4 and show remarkably enhanced visible light harvesting and promoted photo-excited charge carrier separation and transfer. The high-resolution N 1s spectrum of XPS showed a graphitic N peak, which could be attributed to N-doped graphitic carbon. In addition to the common-recognized light harvesting enhancement and charge carrier recombination inhibition, the incorporation of N-doped graphitic carbon into the planar framework of g-C3N4 is suggested to result in extended and delocalized \( p \)-conjugated system of this copolymer, thus greatly elevating the photocatalytic performance for H2 evolution by water splitting under visible light. The H2 evolution rate on N-doped graphitic carbon-incorporated g-C3N4 reached 64 \( \text{mmol h}^{-1} \), which is almost 4.3 times the rate on pure g-C3N4. This approach may provide a promising route for rational design of high performance, cost-effective and metal-free photocatalysts.

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1. Introduction

The ever-increasing demand for clean and renewable energy has stimulated extensive research in the photosynthesis of clean fuels [1]. Semiconductor-based photocatalysis and photoelectrocatalysis hold promise as alternative approaches for solar energy harvesting and storage [2]. As a novel and promising photocatalyst, graphitic carbon nitride (g-C3N4) has sparked significant excitement in energy applications ranging from fuel cells [3,4], supercapacitors [5], electrocatalytic water splitting (HER [6], OER [7]), to photocatalysis for solar water splitting and pollutants photodegradation [8], etc. Besides, g-C3N4 can be applied as a chemosensor for selective optical sensing of metal ions, because its surface exposed terminal amino groups (-NH2 or \( \equiv \text{NH} \) groups) can act as Lewis basic sites [9]. Among its various applications, photocatalysis using g-C3N4 has attracted researchers’ great attention due to its unique physicochemical properties. As an organic semiconductor consisting of carbon and nitrogen, which are among the most abundant elements on the Earth, g-C3N4 is metal-free and sustainable, and can be cheaply obtained from simple precursors like urea, cyannamide, dicyandiamide, melamine, etc. It is featured with 2D conjugated planes, in which tri-s-triazine units periodically repeat themselves, and stacked together through van der Waals interactions. The advantages of g-C3N4, such as high thermal and chemical stability, suitable band gap (\(-2.7 \text{ eV}\)) and simple preparations, are extremely favorable for practical applications in photocatalysis [10,11]. However, its known poor visible-light utilization and fast charge carrier recombination are the serious limitations. Significant progresses have recently been made in the discovery and design of optimized g-C3N4–based photocatalysts by band engineering [12,13], micro-/nano-structure construction [14,15], bionic synthesis [16], co-catalyst combination [17], surface/interface modification [18], etc.

Recently, researchers aimed to extend the light absorption and elevate the charge separation efficiency by copolymerization with organic monomers or constructing polymer–polymer composites [19–22]. Manas et al. incorporated a subtle amount of the pyridine moiety into the g-C3N4 layer structure using a strategy of combining super molecular aggregation with melted ionic
polycondensation, and the apparent quantum efficiency (AQE) of this photocatalyst reached approximately 7% at 420 nm [19]. Chen et al. adopted a molecular doping strategy to incorporate π-deficient pyridine ring entities into the conjugated matrix of g-C3N4 to relocate its π-electrons [20]. Zhang et al. grrafted a variety of aromatic groups on g-C3N4 to extend the delocalization of π-electrons and optimize its photocatalytic performance [21]. Yan constructed composite catalysts of g-C3N4 and poly(3-hexylthiophene) and elevated the H2 evolution rate by up to 300 times [22]. Most recently, the construction of g-C3N4-based intramolecular donor-acceptor conjugated copolymers has been reported by our group, which showed elevated activity of g-C3N4 for hydrogen evolution [23]. It is obvious that copolymerization modification and construction of composite polymer is a smart and efficient way to modulate the intrinsic electronic property and optimize the catalytic performance of g-C3N4. Whereas, we note that all the employed chemicals containing aromatic heterocycles in above reports are not environmentally friendly.

Carbon or graphene composites of photocatalysts have become a hot interest recently, especially carbon quantum dots (CQDs) or graphene quantum dots (GQDs) sensitized semiconductors [24,25]. Recently, Kang and his coworkers reported a very interesting result. They synthesized carbon nanodots/g-C3N4 photocatalyst with impressive performance for solar water splitting [26]. Citric acid, a weak organic acid with three carboxyl groups, is one of the commonly used precursors to synthesize carbon materials through dehydration and carbonization [27,28]. Qu and his coworkers prepared N-doped GQDs using citric acid and urea as carbon precursor and N-containing base, respectively [29]. They believed that citric acid had self-assembled into sheet structure through an intermolecular hydrogen bond between –NH2 and –COOH under the presence of amine, thus N-doped GQDs were obtained. In an earlier report by Schaber et al., urea was found to melt at about 133°C during the pyrolysis, accompanying the decomposition and vaporization [30].

As discussed above, only N-doped GQDs were obtained by hydrothermal treatments using urea-added citric acid as the carbon precursors in the above reports, however, we deduce that urea, the most commonly used precursor for g-C3N4 fabrication, would offer a liquid and amine-rich environment to react or copolymerize with citric acid during the process of high temperature treatment, thus offering an opportunity to yield g-C3N4-base composite.

Here we report, for the first time as far as we know, a facile onepot approach of calcining the mixture of urea and small amount of citric acid for the synthesis of N-doped graphitic carbon-incorporated g-C3N4 composite, in which citric acid played the role of carbon source and reacted with urea to form N-doped graphitic carbon units in g-C3N4 matrix. The as-obtained composites showed remarkably enhanced photocatalytic performance for H2 evolution by water-splitting under visible light.

2. Experimental section

2.1. Chemicals

Urea (AR) was purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China), and citric acid monohydrate (ACS) was obtained from Alfa Aesar. All chemicals were used as received without further treatment.

2.2. Synthesis of photocatalysts

The pure g-C3N4 was prepared by directly heating urea (20 g) at 550°C for 4 h, with a ramp rate of 2°C min⁻¹ in air. The product denoted as CN. The modified samples were prepared by mixing urea (20 g) with different amounts (15 mg, 20 mg, or 25 mg) of citric acid monohydrate, subsequently calcining the mixture in a crucible with a cover at 550°C for 4 h with a ramp rate of 2°C min⁻¹ in air. The obtained samples were denoted as CN-x (x = 15, 20, 25, respectively).

2.3. Characterization

X-ray diffraction measurements were collected on a Rigaku Ultima IV diffractometer (Cu Kα radiation). Fourier transformed infrared (FTIR) spectra were recorded with a Nicolet iS10 FTIR spectrometer. Transmission electron microscopy (TEM) imaging and selected area electron diffraction (SAED) were performed on a JEOL 200CX electron microscope operated at 200 kV. Nitrogen adsorption–desorption isotherms at 77 K were measured on a Micromeritics TriStar 3000 instrument. All the samples were degassed at 150°C for 8 h under flowing N2 before the measurement. Elemental analysis (C, H, N) was performed on a VARIO EL III microanalyzer. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo Scientific ESCALAB 250 spectrometer with Al Kα radiation as the excitation source. Binding energies for the high resolution spectra were calibrated by setting C 1s to 284.6 eV. The UV–vis absorption spectra were recorded on a UV–3600 Shimadzu spectrometer. Photoluminescence spectra (PL) of the samples were obtained at room temperature excited by incident light of 370 nm on FluoroMax®4 fluorescence spectrometer. PL spectra of CN and CN-20 dispersed in deionized water were measured on RF-5301 PC (Shimadzu).

2.4. Photoelectrochemical measurements

Electrochemical measurements were carried out on a CHI 660D electrochemical workstation (CH Instruments, Shanghai, China) with a standard three-electrode cell, which employed an FTO electrode deposited with samples as the working electrode, a platinum sheet as the counter electrode and saturated Ag/AgCl as the reference electrode. Using a 300W Xe lamp (PLS-SEX300C, Perfectlight Limited, Beijing) with a 420 nm cut-off filter as visible light source and 0.2 M Na2SO4 aqueous solution (50 mL) as the electrolyte. The photocurrent was measured at a bias voltage of 0.1 V. The working electrodes were prepared as follows: First, FTO glasses were cleaned by sonication successively with distilled water, acetone and ethanol for 30 min. Then, 4 mg of sample powder CN, CN-15, CN-20, CN-25 was ultrasonically dispersed in 500uL ethanol with 20 ul Nafion solution (5%). One solution without sample powder is used for blank experiment. The resulting dispersion was drop-coated onto the FTO side. Then the electrodes were sealed with epoxy resin except for the 0.25 cm² sample area left for photoreaction experiments, and then dried in air. EIS Nyquist plots were obtained with an amplitude of 5 mV over the frequency range from 10⁵ to 0.01 Hz at a bias voltage of 0V.

2.5. Photocatalytic water splitting test

The visible light-induced H2 evolution was carried out in a Pyrex top–irradiation reaction vessel connected to a closed glass gas-circulation system (Lab-Solar-III AG, Perfectlight Limited, Beijing). A 300 W xenon lamp (CEL-HXF300, Coaulight, Beijing) with a 420 nm cut-off filter was chosen as a visible light source, and the light intensity was 230 mW cm⁻² (tested by FieldMax-II-T0, Coherent®). Photocatalyst (50 mg) was suspended in an aqueous solution (100 mL) containing triethanolamine (10 vol%), and 3 wt% Pt was loaded on the surface of the catalyst by the in situ photo-deposition method using H2PtCl6 as the starting material. The reactant solution was evacuated several times to remove air prior to
the irradiation experiment. The temperature of the reaction solution was maintained at 10 °C by a flow of cooling water during the photocatalytic reaction. The evolved gases were analyzed by gas chromatography (GC7900, Techcomp) equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using nitrogen as the carrier gas.

3. Results and discussion

3.1. Structure and morphology characterization

As shown in Fig. 1a of the XRD patterns of as-synthesized materials, two distinct diffraction peaks are found for all the samples, which can be ascribed to the typical diffraction peaks of g-C₃N₄ (JCPDS 87–1526). The stronger peak at around 27.6° represents the (002) inter-planar graphitic stacking with an interlayer distance of d = 0.322 nm [31]. The other peak at around 12.8° corresponds to the (100) reflection presenting in-plane structural packing motif of tri-s-triazine [32]. The small amount of citric acid addition led to slight change in the location, intensity and shape of these two diffraction peaks, indicating that the samples obtained by citric acid-assisted calcination well retain the molecular framework of pristine g-C₃N₄. Furthermore, the FT-IR spectra in Fig. S1 confirm this conclusion, all of these samples exhibit several typical absorption bands reveal the characteristic structure of g-C₃N₄. The absorption bands located at 1200-1600 cm⁻¹ relate to the stretching modes of aromatic C–N heterocycles; The peak at ca. 807 cm⁻¹ represents the breathing mode of the triazine units; While the broad band at 3000-3500 cm⁻¹ belongs to the N–H vibration due to the surface uncondensed amine groups [33]. However, for these samples CN-x in Fig. 1b, there are two extra peaks sited at 1557 cm⁻¹ and 1635 cm⁻¹, respectively, enhanced with increasing addition of citric acid, suggesting the presence of a C=O skeletal vibration band of aromatic domains [34]. Thus, it can be concluded that this additional carbon species has been co-polymerized into the molecular structure of g-C₃N₄, without changing its original framework because of the ultra-low dosage of citric acid.

In Fig. 1c and d of TEM images, both samples exhibit typical nanosheet structure and CN-20 is more curly at the edge than CN. Their corresponding selected area electron diffraction pattern inserted in Fig. 1c and d also confirms their polycrystalline nature. As mentioned above, citric acid can be used to synthesize CQDs or GQDs through a “bottom-up” approach [35], but in the present study no CQDs or GQDs can be found even under high resolution TEM imaging. Table S1 summarizes the BET specific surface areas and elemental compositions of the obtained samples. It can be inferred that the small amount of citric acid addition can slightly increase the specific surface area of g-C₃N₄, which may be caused by the increased gaseous by-product like CO₂, H₂O. Elemental analysis (C, H, N) was performed to investigate the elemental composition of the samples. As listed in Table S1, the four samples exhibit similar C, H, N contents. Based on the above results, including XRD, FT-IR, TEM and elemental analysis, we can conclude that in the resultant CN-x samples no isolated carbon particles have been formed and the additional carbon species must have been incorporated into the network of g-C₃N₄, without changing its original planar triazine molecular structure.

In order to further reveal the surface chemical compositions of the obtained samples, X-ray photoelectron spectra (XPS) were recorded. The survey spectra in Fig. S2 demonstrate that the two samples CN and CN-20 are mainly composed of C and N elements, in line with the results of elemental analysis. The high-resolution C 1s spectra are shown in Fig. 2a. CN and CN-20 have similar C 1s spectra with two peaks located at about 284.6 eV and 288.1 eV, respectively. In a previous report, the peak at 284.6 eV has been attributed to the signal of C–C bonds of graphitic carbon impurities in g-C₃N₄ [36], while where and how these carbon species were incorporated in g-C₃N₄ were not clarified. The peak with a binding energy of 288.1 eV can be further deconvoluted into two Gaussian-Lorentzian peaks. The main contribution peak at 288.1 eV is attributed to the sp²-hybridized carbon bonded to N atom inside the triazine rings, while the minor peak at 288.8 eV is assigned to the sp²-hybridized carbon in the triazine ring bonded to the amino group [37]. It is worth noting that the two peaks at 284.6 eV (5.89%) and 288.8 eV (13.09%) of sample CN-20 are much stronger.

Fig. 1. (a) XRD patterns and (b) FT-IR spectra (1400-1700 cm⁻¹) of CN and CN-x (x = 15, 20, 25) samples. Typical TEM images of (c) CN-20 and (d) CN. The inset images are the corresponding selected area electron diffraction (SAED) patterns. (A color version of this figure can be viewed online.)
compared to those (284.6 eV: 4.38%, 288.8 eV: 5.71%) of CN. The high-resolution N 1s spectrum of CN-20 is a little different from that of CN as shown in Fig. 2b. The N 1s spectrum of CN can be mainly deconvoluted into four peaks with binding energies at about 398.6 eV, 399.6 eV, 400.7 eV and 404.4 eV. The dominant peak at 398.6 eV corresponds to the sp2-hybridized nitrogen in C-containing triazine rings (C=N=C), whereas the peak located at 399.6 eV is usually attributed to the bridging N atoms in N-(C)3 groups. The peak at 400.7 eV indicates the amino groups (N–H), and the peak at 404.4 eV is attributed to charging effects [38]. In sample CN-20, an extra peak located at 401 eV, which corresponds to the graphitic N (Fig. S3) [39], can be observed, indicating that N-doped graphitic carbon has been formed and introduced into the g-C3N4 matrix. This can be further confirmed by the enhanced graphitic C–C signal at 284.6 eV (5.89%) in C 1s spectrum of CN-20.

TG curves obtained during the thermal polymerization of urea and urea/citric acid mixture are shown in Fig. S4. It can be observed that the addition of citric acid leads to the less weight loss above the melting point (~132.7 °C) of urea, implying that reaction/condensation has taken place between citric acid and urea. Considering that carboxyl groups of citric acid can react with amine groups of urea, the copolymerization between citric acid and urea will take place during the calcination process to form N-doped graphitic carbon, which could be dangled onto the surface or inserted in tri-s-triazine network of g-C3N4 matrix (Fig. 3). However, because of the ultra-low dosage of citric acid and the similar properties of g-C3N4 and N-doped graphitic carbon, it’s hard to distinguish N-doped graphitic carbon from the g-C3N4 matrix based on XRD, Raman spectra (Fig. S5) and even NMR [26,40].

3.2. Optical properties and electronic band structures

The optical properties of the as-prepared samples were qualitatively probed by UV–vis diffuse reflectance absorption and photoluminescence (PL) spectroscopy, as shown in Fig. 4. The UV–vis diffuse reflectance absorption spectra in Fig. 4a indicate that the intrinsic absorption edge (that is, band gap) of CN-x red-shifts a little in comparison to that of CN. At the same time, the absorption spectra of CN-x samples extend to the whole visible
light region, namely, their light absorbance has been remarkably enhanced. The photograph inserted in Fig. 4a depicts the color change of the photocatalysts from light yellow to brown yellow (in the web version) with the increase of citric acid addition, corresponding to their gradually expanded absorption band and enhanced visible light harvesting. For CN-x samples, N-doped graphitic carbon was formed in g-C3N4 matrix, and the lone pair electron on graphitic N may trigger the p-electron delocalization in this conjugated system, which is most probably responsible for their enhanced photoabsorption and photoresponsivity [41].

The photoluminescence (PL) spectra were obtained by monitoring at an excitation wavelength of 370 nm, and are shown in Fig. 4b. The pure sample CN shows a strong emission peak at ca. 460 nm, while an apparent fluorescence quenching is observed for CN-x, indicating the suppressed recombination among photo-generated charge carriers in CN-x. Simultaneously, the emission peaks of CN-x shifts toward longer wavelength compared to that of CN (from 450 nm to 470 nm). The red shift of both the band gap and PL peak of CN-x (x = 15, 20, 25) may be ascribed to the incorporated graphitic N, which could promote the p-electron delocalization of g-C3N4 network.

We further measured the PL spectra of CN and CN-20 dispersed in deionized water at different excitation wavelengths according to the UV–vis absorption spectra. In Fig. 4c, the typical absorption peak located at 325 nm can be attributed to the intrinsic absorption of g-C3N4 [42], and the absorption shoulder peak at about 250 nm can be assigned to the π–π* transition [43]. Fig. 4c and d shows the PL emission spectra of CN and CN-20. The emission peaks of the two samples are excitation-independent. Compared with the PL peak at 440 nm of CN in Fig. 4d, the emission peak at 470 nm of CN-20 (Fig. 4c), which corresponds to the band–band transition emission (HOMO–LUMO transition), shows a large red shift, which is in accordance with the above characterizations. Two peaks at 360 nm and 400 nm become standout when the excitation wavelength moves to deep ultraviolet light (240–270 nm), indicating that the more electrons must have been excited to higher orbital or inner shell electrons have been excited [44]. Associated with the absorption peak at about 250 nm, which is attributed to the π–π* transition, excitation of 250 nm can result in the strongest emission peak at 360 nm, so we infer that 250 nm is the best excitation wavelength. Meanwhile, considering that the energy gap of π–π* transition is larger than that of n–p* transition, we conclude that the PL peaks at 360 nm and 400 nm can be ascribed to the radiative recombination of π-electrons by the incorporation of N-doped graphitic carbon, and consequently the increased probability of π–π* transition and radiative recombination as well. Such a phenomenon is in consistence with the increased transient photocurrent of the composite compared to pristine CN.

3.3. Photocatalytic activity and catalytic mechanism

H2-evolution by visible light-induced water splitting was carried out to evaluate the photocatalytic performance of these samples. 3 wt% Pt and 10 vol% triethanolamine were used as co-catalyst and hole sacrificial agent, respectively, under visible light irradiation (λ > 420 nm). As illustrated in Fig. 5a, CN-x samples show remarkably enhanced hydrogen evolution performance. The average H2 evolution rate of CN-20 reaches 64 umol h−1, which is almost 4.3 times that of CN (15 umol h−1). The stability of CN-20 was also performed by repeating the photocatalytic experiment under the same condition for four cycles (24 h). As shown in Fig. 5b, there is no significant decrease in the H2 evolution rate after four
cycles, confirming the high stability of this g-C3N4 modified with N-doped graphitic carbon in photocatalytic reaction. CN-20 before and after the recycling experiment of H2 evolution were checked by FT-IR spectra (Fig. S8). No spectroscopic change can be detected, indicating its excellent chemical stability during the photocatalysis process.

The transient photocurrent responses of the as-obtained samples were measured to study the excitation and transfer of photo-generated charge carriers for several on–off cycles under visible-light irradiation, which are plotted in Fig. 5c. All the samples exhibit prompt photocurrent responses on each illumination. As expected, CN-x samples show much enhanced photocurrent response, and CN-20 possesses the highest photocurrent intensity, whereas CN displays the lowest value among all the samples, indicating that CN-20 is the most effective in charge separation, which is in line with its highest photocatalytic activity. The electrochemical impedance spectra (EIS) were recorded to investigate the (photo)electrochemical properties of CN and CN-20. The EIS Nyquist plots of CN and CN-20 electrodes in a 0.2 M Na2SO4 aqueous solution in the dark are shown in Fig. 5d. Both of the Nyquist plots exhibit semicircle-like curve and the diameters are used to assess the impedance. Much smaller semicircle can be observed for CN-20, reflecting that the incorporation of N-doped graphitic carbon can efficiently reduce the charge transfer resistance at the material surface/interface [21]. This suggests a strongly improved electronic conductivity in the non-photoexcited state and would be very beneficial for photoexcited charge separation during photocatalysis. Both photocurrent and EIS experiments prove the incorporation of N-doped graphitic carbon can obviously facilitate charge carrier separation and transfer in these photocatalysts.

Based on the above characterizations and discussions, this N-doped graphitic carbon incorporated with g-C3N4 demonstrate similar surface area and morphology to the pristine. More importantly, the lone pair electron on the graphitic N atom leads to effectively extended and delocalized aromatic π-conjugated system, which has been confirmed by the strengthened PL emission peak at 360 nm and 400 nm due to the enhanced radiative recombination of π-π* and n-π* transition by the incorporation of the N-doped graphitic carbon.

4. Conclusions

In conclusion, N-doped graphitic carbon-incorporated g-C3N4 photocatalysts have been successfully obtained through a facile one-pot thermo-induced polymerization strategy by introducing slight amount of citric acid into urea. The N atom doping in graphitic carbon of the composite is believed to be responsible for extended and delocalized aromatic π-conjugated system of g-C3N4 and consequently much promoted separation and transfer of charge carriers, which, together with the improved visible light harvesting and inhibited charge carrier recombination, resulted in remarkably enhanced photocatalytic H2 evolution activity by water splitting under visible light. The H2 evolution rate on an optimized N-doped graphitic carbon-incorporated g-C3N4 photocatalyst (CN-20) reached 64 μmol h⁻¹, which is almost 3.3 times higher than that of the pristine g-C3N4. This work may offer a new promising route for the rational design and synthesis of high performance metal-free photocatalysts from simple, inexpensive and environmental friendly precursors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.12.008.

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