

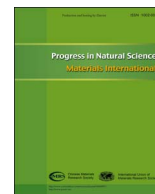
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Original Research

Improving the photocatalytic activity of graphitic carbon nitride by thermal treatment in a high-pressure hydrogen atmosphere

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ABSTRACT

Extending visible light absorption range and suppressing the recombination of photogenerated charge carriers are always important topics in developing efficient solar-driven photocatalysts. In this study, the thermal treatment process at 400 °C in a high-pressure hydrogen atmosphere was applied to modify graphitic carbon nitride. Compared to the normal atmospheric hydrogen treatment process, this process has the merit of producing nitrogen deficient graphitic carbon nitride in high-yield. The optimal photocatalytic activity of modified graphitic carbon nitride was demonstrated by controlling the treatment duration in the hydrogen atmosphere. The changes in the crystal structure, microstructure and optical properties of carbon nitrides were investigated by several characterizations. The relationship between the photocatalytic activity and structures of graphitic carbon nitride was preliminarily established. The results obtained in this study could provide some new ways of improving the activity of graphitic carbon nitride based photocatalyst.

1. Introduction

Developing efficient photocatalysts for solar fuel production, e.g., H₂ production from photocatalytic water splitting and conversion of CO₂ to chemical fuels such as CO, CH₃OH, CH₄, etc., has attracted increasing attention [1–4]. Concerning the utilization of visible light with its wavelength spanning from 400 to 700 nm, which takes a large portion of around 45% in solar spectrum, the wide spectrum responsive photocatalysts have been actively explored. Polymeric graphite carbon nitride (namely, the widely called “g-C₃N₄” in literature, which actually contains about 2 wt% hydrogen from the incompletely condensed NH/NH₂ groups on the basis of most polymerization routes) has emerged as a very promising metal-free semiconductor photocatalyst due to the merits of low cost, good chemical and photocatalytic stability, and favorable optical/electronic features [5–10]. The carbon nitride has a bandgap of around 2.7 eV and appropriate band edges for water splitting to produce hydrogen and oxygen. Although the carbon nitride shows photocatalytic activity in H₂ generation under visible light irradiation, it always suffers from both the narrow visible light absorption range and high recombination probability of photogenerated

charge carriers. These limitations are intrinsically controlled by the relatively large bandgap, low mobility of charge carriers, and also large barriers for the diffusion of charge carriers in g-C₃N₄.

The actively used strategies of increasing visible light absorption of carbon nitride mainly include doping with appropriate nonmetal heteroatoms and introducing defects by controlling the preparation conditions (increasing the polymerization temperature, post-treating in the reductive or inert atmospheres) [11–22]. It was recognized that the layered structure itself favors the homogeneous modification of materials by allowing the diffusion of dopant or reductive species from surface into bulk. Our previous study showed that the homogeneous modification of carbon nitride with nitrogen vacancy was achieved by heating carbon nitride in an atmosphere of the hydrogen flow [23]. The resultant nitrogen deficient carbon nitride with a narrowed bandgap of 2.03 eV had a greatly extended visible light absorption range and improved photocatalytic activity in decomposing dyes. Further study by Tay et al. also showed the enhanced visible light absorption and photocatalytic hydrogen evolution by introducing nitrogen defects in carbon nitride that was produced by directly conducting the thermal polymerization in the hydrogen flow [24]. These treatments were

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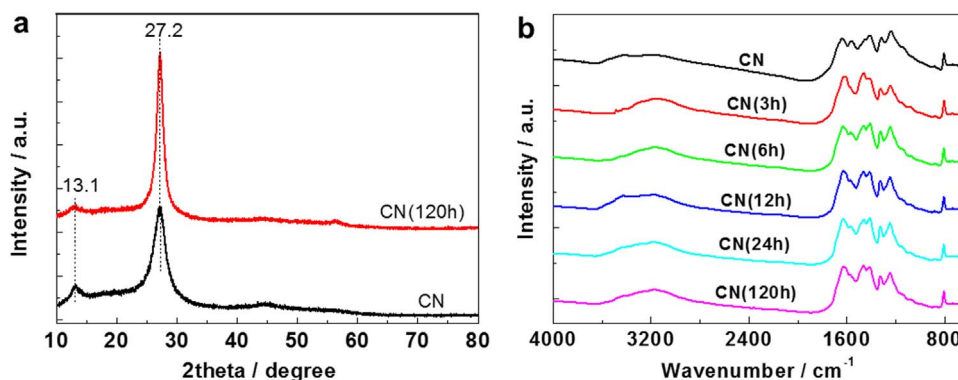


Fig. 1. a, XRD patterns of the CN and CN(120 h) samples; b, FTIR spectra of CN, CN(3 h), CN(6 h), CN(12 h), CN(24 h) and CN(120 h).

usually conducted at the temperature of around 550 °C, which is close to the thermal decomposition of carbon nitride, so that the product yield was usually very low (< 10 wt% yield in the study of Niu et al.). On the other hand, controlling the texture to form ultrathin sheets or porous structures has demonstrated the substantial role in lowering the recombination probability by shortening the diffusion length of charge carriers for improved photocatalytic activity [25–27]. Therefore, the synergistic controlling of both the band structure and microstructure of carbon nitride is highly desirable but challenging.

A high-pressure environment is always favorable for the proceeding of reactions at the relatively medium temperature and sometimes causes some unusual changes. One example in the preparation of photocatalysts is that heating anatase TiO₂ nanoparticles in a 20-bar hydrogen atmosphere at 200 °C for 5 days produced an interesting black TiO₂ photocatalyst [28]. Inspired by this result, in this study we treated carbon nitride bulk in a 50-bar hydrogen atmosphere at 400 °C to produce a series of nitrogen deficient carbon nitride with porous structure. The optimal visible light photocatalytic activity was reached by controlling the amount of nitrogen vacancies and microstructure of carbon nitride. The advantage of the high-pressure atmosphere treating in controlling both the structure and composition of photocatalysts for improved activity was clearly demonstrated.

2. Experimental section

2.1. Sample preparation

Graphitic carbon nitride was prepared by the polymerization of dicyandiamide in static air at 500 °C for 4 h in a muffle furnace. The ramping rate was 2 °C/min. The resultant yellowish agglomerates were milled into powder in a mortar. To prepare the hydrogen-treated carbon nitride, the pristine carbon nitride powder was isothermally heated at 400 °C under an initial H₂ pressure of 5 MPa for varied times from 1 h to 120 h using a homemade Sievert's type apparatus. The pristine and hydrogen-treated carbon nitriles were denoted CN and CN (x) (x = 3, 6, 12, 24 and 120 h referring to treatment time), respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2400 diffractometer using Cu K α irradiation with the wavelength of 1.54056 Å. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27. The composition and chemical state of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, monochromatic Al K α X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) that arises from adventitious carbon. Elemental analysis (EA) was performed on a Vario MICRO instrument (Elementar, Germany). The N₂ absorption-desorption isotherms were determined at 77 K with a Micromeritics ASAP

2010. The transmission electron microscopy (TEM) images were obtained by a JEOL 2010 electron microscope. Electron spin resonance (ESR) spectra were measured using a Bruker ESP300E spectrometer. The optical absorption spectra were recorded on a UV-visible spectrophotometer (JASCO-550) in the diffuse reflectance mode. Photoluminescence (PL) emission spectra (385 nm excitation) were measured at room temperature with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920).

2.3. Photocatalytic H₂ generation measurement

Photocatalytic hydrogen generation reactions were carried out in a top-irradiation vessel connected to a glass gas circulation system. 50 mg of the photocatalyst powder was dispersed in 300 mL of the aqueous solution containing 10 vol% triethanolamine as a sacrificial reagent. The deposition of 6 wt% Pt co-catalyst was achieved by dissolving H₂PtCl₆ in the above reaction solution and subsequent light irradiation. The reaction temperature was kept around 10 °C. The amount of H₂ generated in the reaction was determined using a gas chromatograph (Agilent 6890). The light source was a 300 W Xe lamp (Perfectlight Sci&Tech Corp Ltd., PLS-SXE-300UV) and the incident visible light was obtained by using a 420 nm cutting-off glass filter to remove UV light.

3. Results and discussion

The high-pressure hydrogen atmosphere treatment performed at 400 °C in this study led to a high product yield of around 50 wt%, which was far higher than that of < 10 wt% for an atmospheric hydrogen pressure treatment performed at 540 °C. The combined results derived from X-ray diffraction (XRD) patterns and Fourier Transform Infrared (FTIR) Spectra clearly suggest the good retaining of basic atomic structure of graphitic carbon nitride samples obtained at different treatment durations. Fig. 1a exhibits the XRD patterns of the CN and CN (120 h) samples. Two typical diffraction peaks of graphite-like layered carbon nitride centered at around 13.1° and 27.2° are originated from the in-plane packing motif of tri-s-triazine units and the interplane periodic stacking of the layers along c-axis, respectively. The comparison of the patterns of two samples shows no obvious position shift but changed intensity of two peaks. The enhanced intensity of the peak of 27.2° and obviously weakened intensity of the peak of 13.1° indicate the increased long-range ordering packing along c-axis and decreased short-range ordering in the in-plane packing, respectively. These changes can be well understood from two aspects. The thermal effect favored the increased crystallinity by regulating the atomic long-range ordering towards a better packing of the building block sheets. On the other hand, the reductive atmosphere caused the loss of some nitrogen atoms from the framework of carbon nitride so that the in-plane long-range ordering of the atoms was destroyed, as also demonstrated in the previous studies [21,22].

The FTIR spectra of all samples in Fig. 1b show no essential change

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