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KOH etching graphitic carbon nitride for simulated sunlight photocatalytic nitrogen fixation with cyano groups as defects

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ABSTRACT

Cyano-deficient g-C_3N_4 (graphitic carbon nitride, labeled GCN) was synthesized by KOH etching treatment of bulk g-C_3N_4. Characterization results indicated that KOH etching treatment had a certain effect on the morphology and structure of GCN, and successfully introduced the cyano groups into GCN framework. The obtained KOH etching g-C_3N_4 catalysts, named ACN, exhibited the pore and/or ladder-like thin layered structure. Meanwhile, the introduction of cyano groups reduced the conduction band position of ACN, and effectively inhibited the recombination of photo-generated electron–hole pairs. In addition, ACN introduced more chemical adsorption sites to activate nitrogen, which was beneficial to the reaction of photocatalytic nitrogen fixation. The modification of morphology and electronic property, especially the introduction of cyano functional groups, remarkably promoted the activity of ACN on the simulated sunlight photocatalytic nitrogen fixation, which was 7.6-fold higher than that of GCN.

1. Introduction

The conversion of solar energy into chemical energy, such as hydrogen and ammonia, is an effective way to solve global energy and environmental problems. The photocatalytic fixation of nitrogen to ammonia has gradually attracted attention due to its advantages of mild conditions, low power consumption and low cost. Thus, it is considered to be a promising method to replace traditional industrial nitrogen fixation techniques. Schrauzer and Guth first reported the formation of ammonia over Fe-doped titanium dioxide under UV light irradiation in 1977 [1]. Since then, most of the researches on nitrogen photofixation are focused on the modification of TiO_2 to improve the efficiency [2–4]. Other photocatalysts, such as modified $SrTiO_3$ [5], Fe @ 3D Graphene [6] and BiOBr [7], *etc*., had also been found to be useful for nitrogen fixation under light irradiation at ambient temperature and pressure.

Graphitic carbon nitride (g-C_3N_4, labeled GCN), which was used for photocatalytic hydrogen evolution experiments for the first time in 2009 [8], has been utilized as a low-cost, sustainable, metal-free, and visible-light-active photocatalyst in the field of solar energy conversion in recent years [9–11]. To further improve its photocatalytic performance, many approaches, such as morphology control [12,13], band-gap engineering (including element doping [14,15] and copolymerization [16,17]), and coupling with other semiconductors [18,19], have been reported extensively.

The introduction of defects in semiconductor materials is considered to be an effective way to improve the photocatalytic activity, because defects can modify the electronic structure and trap photo-generated electrons or holes to inhibit the recombination of photo-generated carriers. It has been reported that oxygen vacancies on TiO_2 could trap electrons and enhance photocatalytic performance of TiO_2 in the visible range [20,21]. Similarly, Niu et al. [22] has reported that the nitrogen vacancies were introduced into the framework of GCN by a simple temperature-controlling route and modified the electronic structure to improve the photocatalytic activity of GCN. Dong et al. [23] investigated the role of nitrogen vacancies in nitrogen heat-treated GCN for N_2 photofixation under visible-light irradiation. The result indicated that the N_2 was selectively adsorbed and activated on the nitrogen vacancies and photo-generated electrons could also be trapped to inhibit the recombination of photo-generated charge carriers. Hong et al. [24] developed a facile hydrothermal strategy using ammonium thiosulfate as a weak oxidant to prepare nitrogen-deficient GCN, and the results revealed that the deficiency of amino species on GCN was beneficial to light harvesting and separation of charge carriers. A template-free method using different solvents (such alcohols) to pretreat the precursor had been reported to synthesize sponge-like GCN with a large surface area and nitrogen vacancies [25]. In recent year, the effects of different defects on the

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photocatalytic reaction, such as oxygen vacancies [26], carbon vacancies [27], sulfur vacancies [28], and defects caused by catalyst morphology or surface functional groups [29,30], have also been further studied. It is noteworthy that there are some reports on the impact of nitrogen vacancies on the activity of photocatalysts [22,24,25,31–34], but little about cyano defects. In theory, cyano groups as a strong electron acceptor may act as defects. Ou et al. [30] and Yu et al. [35] also have reported that the presence of cyano groups could effectively improve the photocatalytic hydrogen performance of carbon nitride. Based on those, cyano groups as a defect may have an effect on photocatalytic nitrogen fixation.

In this work, we successfully prepared cyanide-deficient carbon nitride (ACN) via KOH etching treatment of bulk GCN. The simulated sunlight nitrogen photofixation ability was tested to evaluate the performance of photocatalysts. The results indicated that the cyano defects contributed to the separation of photo-generated carriers and significantly improved the nitrogen fixation capacity of ACN. This work reported a facile and effective way to introduce cyano groups into GCN and discussed in detail the impacts of cyano deficiency on the morphology, structure and optical properties of ACN.

2. Experiment

2.1. Material synthesis

The pristine GCN was prepared by heating melamine in a muffle furnace at 550 °C for 4 h with a ramp rate of 2 °C/min in air. The KOH etching graphitic carbon nitride (ACN) was synthesized as follows: the as-prepared GCN powder was dispersed in anhydrous ethanol containing an appropriate amount of KOH. Solvents were removed by evaporation at 70 °C with vigorous stirring. The obtained powders were heated to 500 °C under flowing nitrogen and held there for 2 h in a horizontal tube furnace. After cooling down, the resultant samples were repeatedly washed by deionized water until neutral pH was reached. Finally, the product was dried at 60 °C overnight. The obtained catalysts were denoted as ACN-x (x = 2%, 5%, 10%), where x stands for the mass ratios of KOH to GCN.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the photocatalysts were recorded on a Bruker D8 Advanced diffraction-meter with Cu Kα radiation and with the scanning angle ranging from 10° to 80°. The scanning electron microscopy (SEM) images were obtained on Quant 250FEG instrument and the transmission electron microscopy (TEM) images were measured on TECNAI G2 20 (LaB6). The nitrogen adsorption isotherms at 77 K were measured on Micromeritics ASAP 2200. The samples were degassed at 523 K prior to measurements. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated based on the adsorption isotherm. The Fourier transform infrared (FT-IR) spectroscopy was carried on a Nexus 870 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV). Elemental analysis (EA) data were obtained by using EuroVector EA3000. UV–vis diffuse reflectance spectroscopy was carried out on a Hitachi U-3010 UV–vis spectrometer. Photoluminescence (PL) spectra were measured at room temperature with a jobinYvon SPEX Fluorolog-3-P spectroscope. The photocurrents were measured using an electrochemical workstation (CHI 660E) in a standard three-electrode system under illumination using a 300 W Xe lamp. The catalyst coated ITO glass was used as the working electrode, a Pt foil was used as the counter-electrode, and an Ag/AgCl electrode was used as the reference electrode. A 0.5 M Na_2SO_4 aqueous solution was used as the working electrolyte. N_2-Temperature programmed desorption (N_2-TPD) was performed using a CHEMBET-3000 (Quantachrome, U.S.A.) instrument in the temperature range of 313–1073 K. The Electron paramagnetic resonance (EPR) spectra were conducted on a Bruker EMX-10/12 EPR.

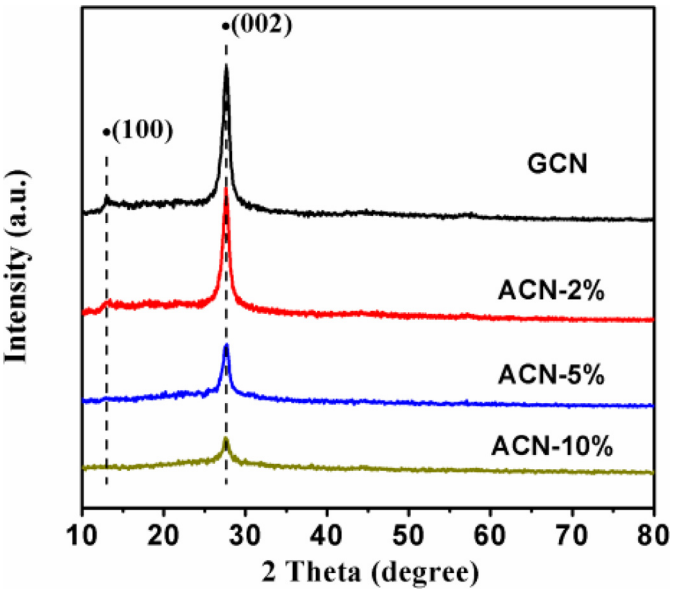

Fig. 1. XRD patterns of GCN and ACN-x.

2.3. Photocatalytic experiment

The photocatalytic nitrogen fixation experiments were performed in a double-walled quartz reactor in air. For these experiments, 0.1 g of the photocatalyst powder was suspended in 200 mL aqueous solution containing 10 vol % methanol as scavenger. During the reaction, a 500 W Xe lamp was used as simulated sunlight source (the light intensity on quartz tube was 7.66 mW/cm^2) and air was used as N_2 source. At given time intervals, 2.5 mL of the reaction solution was sampled and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentration of ammonia was measured using the Nessler's reagent spectrophotometry method (HJ 535–2009) with a VIS-7220 spectrophotometer.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of GCN and ACN-x photocatalysts are shown in Fig. 1. The bulk GCN contains two pronounced diffraction peaks at around 27.6° and 13.0°, the former can be indexed as the (002) peak characteristic for interlayer stacking of aromatic systems, and the latter can be indexed as the (100) peak that corresponds to the in-plane repeating motif [36]. After KOH etching, the ACN-x photocatalysts have the same crystal phases as pristine GCN. However, in comparison with the pristine GCN, the intensities of the (002) peak of ACN-x are significantly reduced with increasing KOH usage, which suggests the deterioration of crystallinity after KOH etching. The (100) peak diffraction of ACN-2% and ACN-5% becomes weaker and broader, and that of ACN-10% even disappears, indicating that the ordered arrangement of tri-s-triazine units is broken or changed and some defects may exist in ACN-x framework [23,25].

The morphological structures of the samples were examined by SEM and TEM analysis. From the SEM images in Fig. 2a, the bulk