



Steam engraving optimization of graphitic carbon nitride with enhanced photocatalytic hydrogen evolution

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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) has been extensively investigated as an efficient photocatalyst for water splitting. However, the intrinsic drawbacks of low surface area and poor charge separation efficiency seriously limit its practical applications in photocatalytic hydrogen evolution. Here, we designed an efficient nanorod-C₃N₄ photocatalyst by a versatile and scalable steam engraved protocol, which can produce higher surface area, enhanced crystallinity, reduced lattice defects, as well as meliorative energy band configuration. The engraved C₃N₄ exhibited a remarkably longer lifetime of charge carriers and a much higher photocatalytic hydrogen production rate than the pristine C₃N₄. The specific activity of the engraved C₃N₄ (87 μmol g⁻¹h⁻¹cm⁻²_{BET}) is 10.4 times higher than that of pristine C₃N₄.

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1. Introduction

Environmental and energetic crisis have been gained considerable interdisciplinary attention recent years. Hydrogen is an ideal alternative energy source as substitute for fossil fuels and is currently considered to represent a clean and renewable future energy source. Solar-driven photochemical, in which water is splitted to produce hydrogen and oxygen using semiconductor photocatalyst, is a potential mean of directly obtaining renewable hydrogen [1]. Therefore, searching and optimizing highly efficient photocatalysts have invigorated growing awareness.

Since Wang et al. first reported the pioneering study that using graphitic carbon nitride (g-C₃N₄, CN) as photocatalyst to drive water splitting in 2009 [2], the graphite-like metal-free layered material with a visible-light driven bandgap (~2.67 eV) and proper band edges has emerged as a new class of photocatalyst [3,4], especially for water splitting under sunlight irradiation [5,6]. In fact, the photocatalytic activity of C₃N₄ is mainly affected by its surface area and crystallinity. Higher surface area can provide more

accessible sites for photochemical reactions, while the eliminating grain boundary defects on modified C₃N₄ with high crystallinity could significantly decrease the photoexcited charge carrier recombination [7]. The crystallinity and nitrogen content of the carbon nitride was mainly dictated by the polymerization degree of the nitrogenous precursors. However, the bulk g-C₃N₄ synthesized by calcining melamine at high-temperature usually shows a relatively low photocatalytic activity, which can be ascribed to the imperfect C₃N₄ crystallinity forming by the incomplete deamination or polymerization of the precursor [8].

At present, many strategies, such as band gap engineering [9,10], surface carbon defects designing [11], heteroatoms introducing [12] [13], morphology controlling [14], semiconductors coupling [15], have been used to improve the photoactivity of C₃N₄ to satisfy the needs of practical applications [16,17]. However, few studies have been performed focusing on the structure engineering that constructing higher surface area and simultaneously reducing the boundary defects of the carbon nitride. Recently, except from non-metal [18] and metal dopant [19,20], a simple methanol reflux method was proposed to increase the active lattice face and eliminate surface defects [7]. In addition, 1,3,5-cyclohexanetriol was used to manipulate the structure engineering process suggested by Yu et al. [21]. However, the extra organic additives required and

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difficult handling conditions make each of these strategies more complex.

Herein, we designed a highly crystalline C_3N_4 with higher surface area and reduced lattice defects by the steam engraved strategy. The pristine C_3N_4 was separated with water by a crucible and further hydrothermal treatment under assigned temperature and period, as illustrated in Scheme 1. It is well known that the water is often used for exfoliation of C_3N_4 into single or few layered C_3N_4 under ultrasonic conditions for dozens of hours, and it could effectively engrave the C_3N_4 to nanosheets structure with more surface sites exposed [22,23]. However, more surprisingly, in our case, the optimally treated C_3N_4 exhibits rod morphology (labelled as Rod- C_3N_4 , while the pristine C_3N_4 was labelled as Bulk- C_3N_4 for comparison) with enhanced surface area, reduced defects, meliorative energy band configuration.

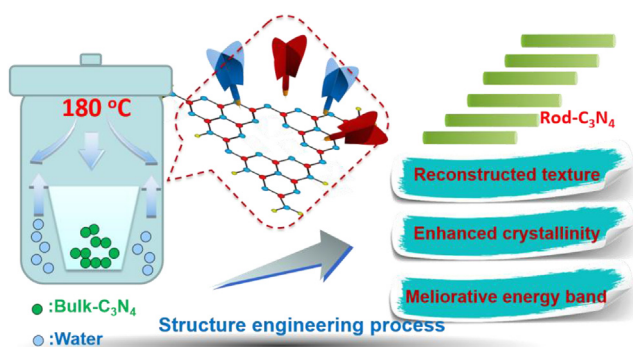
2. Results and discussion

2.1. Reconstructed texture

A reconstructed texture is observed by structure engineering process. Fig. 1a and b show the SEM images of pristine and treated C_3N_4 . A massy morphology is observed for pristine C_3N_4 (Fig. 1a and Fig. S1), while the engraved sample shows mainly in nanorods shape (Fig. 1b). When the engraved time is controlled up to 12 h, the Rod- C_3N_4 are 0.5–1 μm in length and 100–150 nm in diameter (Fig. 1c). The HRTEM shows a distinct interplanar spacing with 0.209 nm marked in Fig. 1d corresponding to the (002) plane of Rod- C_3N_4 , which is lower than that of traditional C_3N_4 (0.325 nm), indicating that the Rod- C_3N_4 has higher crystallinity. Obviously, it can be seen that the water-engraved C_3N_4 have a much higher surface area per unit mass. To confirm this hypothesis, the N_2 adsorption-desorption isotherms (Fig. 1e) are obtained for the two samples. The Brunauer-Emmett-Teller (BET) surface area of steam-engraved C_3N_4 is much higher than that of pristine C_3N_4 (21.1 vs. 8.3 $\text{m}^2 \text{g}^{-1}$).

2.2. Enhanced crystallinity

XRD characterizations (Fig. 2a) were performed to observe the crystalline change before and after the steam treatment. Both C_3N_4 have distinct diffraction peaks at 27.4° , which can be indexed as (002) diffraction for graphitic C_3N_4 materials, representing interfacial stacking of g- C_3N_4 sheets. The diffraction peak at 13.0° can be indexed as (100), representing in-plane packing. These two diffraction peaks show that C_3N_4 still remained a layer structure after steam engraving. Compared with the pristine one, the (002) diffraction peak of Rod- C_3N_4 shifts to higher angle after treatment,



Scheme 1. Illustration of the structure engineering process for constructing Rod- C_3N_4 .

indicating a slight decrease in interlayer stacking distance and an increase of interlayer stacking density cause by the steam engraving. These results are highly agreed with previous studies [7,24]. In addition, the narrower and sharper peaks suggest that steam can react with pristine C_3N_4 during the engraving process, causing the increase of ordered structures within the framework [8,25]. More surprisingly, a new peak at 6.3° , attributed to the crystal plane (001), is appeared after steam engraving. The diffraction peaks at about 11 , 20 – 26 and 31° are observed for Rod- C_3N_4 , while no peak showed at this position for Bulk- C_3N_4 . According to the study by Bai et al. which show a simple methanol reflux method to construct a higher crystallinity C_3N_4 , the diffraction peaks at about 11 , 20 – 26 and 31° implied a high purity and crystallinity of Rod- C_3N_4 [7].

The chemical structure changes were analyzed by FTIR spectra, as presented in Fig. 2b. The basic atomic structure shows no obvious change since both samples exhibit the typical IR patterns of g- C_3N_4 [5,25]. A broad peak at around 3000 – 3500 cm^{-1} for the stretching vibrations of $-\text{NH}_x$ and $-\text{OH}$ reveal the existence of primary/secondary amines and surface absorbed water. Meanwhile, the sharp absorption band centered at 810 cm^{-1} originating from the breathing mode of triazine units indicates the existence of the basic melon units with $-\text{NH}/-\text{NH}_2$ groups [24,26]. Additionally, the bands observe in the region of 900 – 1800 cm^{-1} are the typical vibrations of C-N and C-N-C bonds, which associates with the skeletal stretching modes of aromatic rings [27]. Obviously, the peak at 810 cm^{-1} shifts toward higher frequency after steam engraving, suggesting the enhanced crystallinity of Rod- C_3N_4 [24]. Both XRD and IR results indicate that the intrinsic structure of C_3N_4 is not changed by steam engraving, although a better crystallinity of C_3N_4 was obtained.

Different treating time was also investigated to optimize the engraved conditions and the XRD, IR and SEM results are shown in Fig. S2–S4 in supporting information. It can be found that the crystallinity of C_3N_4 increased with increased engraving time, as indicated by the enhancing intensity of the typical XRD peaks over time in Fig. S2. In addition, the peak at around 810 cm^{-1} in the FTIR results gradually shift toward higher frequency (Fig. S3) as treated time increased, which also illustrating the increased crystallinity of C_3N_4 [24]. It is interesting that the morphology becomes more pronounced and partially longer when the engraving time was lengthened to 24 h or 48 h (Fig. S4). We assume that the morphology alteration from an irregular C_3N_4 to Rod- C_3N_4 type and further to larger clavate-like structure may be due to an exfoliation and regrowth process, which could eliminate the lattice defect and enhance the surface area of pristine C_3N_4 . No obvious structure transform from pristine to better crystallinity was occurred under 140°C till 24 h steam engraving (Fig. S5), indicating that the degree of engraving is temperature and time dependent.

Since the photocatalysis reaction mainly occurs on the catalysts surface, it is essential to investigate the surface properties of C_3N_4 before and after high temperature water treatment. In addition, it is crucial to illustrate the merit of this lattice engineering process. In XPS results, the survey spectra (Fig. 2c and d and Fig. S6) show the presence of C, N and O in both samples. The fine-scanned C 1s, N 1s and O 1s XPS spectra of the pristine and engraved C_3N_4 exhibit a similar peak tendency. That is, the chemical composition and coordination of carbon and nitrogen in Rod- C_3N_4 are retained during the steam-engraving process, which is highly agreed with the XRD and IR results. Compared to pristine C_3N_4 (C/N = 0.52), the Rod- C_3N_4 exhibits a lower C/N molar ratio of 0.44, as analyzed by elemental analysis (Table S1). For C 1s spectra (Fig. 2c), the peaks at 284.6 and 287.4 eV arise from sp^2 -hybridized C-C bonds and sp^2 -hybridized C in aromatic skeleton rings of C_3N_4 (N-C=N), respectively [3,28]. Obviously, the C1s binding energy of N-C=N shifts

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