



## Research paper

# Microstructure of carbon nitride affecting synergetic photocatalytic activity: Hydrogen bonds vs. structural defects



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## ABSTRACT

Carbon nitride has emerged as one of the most attractive materials for developing photocatalysts with low cost, high efficiency and structural stability. However, fast charge recombination caused intrinsically by the  $\pi$ - $\pi$  conjugated electronic system severely limits its photocatalytic performance. Constructing carbon nitride photocatalysts with modulated electronic structures is thus a promising but challenging task. In this paper, carbon nitride with different microstructural features, such as degree of polymerization, hydrogen bonds, bandgap, structural defects and ratio of C/N, were synthesized by polymerization of different types of nitrogen-rich precursors. Synergetic reactions were rationally designed for hydrogen production and the efficient and simultaneous removal of multiple contaminants, using carbon nitrides as metal-free photocatalysts. The significant impact of hydrogen bonds on synergetic photocatalysis was comprehensively demonstrated. With the smallest amount of hydrogen bonds, carbon nitride derived from urea exhibited fast charge transfer between interlayers, which is a prerequisite for superior photoactivity. By contrast, the polymerization of melamine and cyanamide was favorable for the formation of abundant hydrogen bonds and intrinsic vacancy defects. It was found that the coexistence of nitrogen deficiency and oxygen-doped microstructures could facilitate the activation of oxygen molecules, and thereby contributed to their moderate photoactivity. This research provides fundamental insights into the microstructural engineering of carbon nitride for high-performance synergetic applications.

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## 1. Introduction

To date, the exploration of abundant, sustainable and efficient metal-free photocatalytic materials is especially attractive but challenging [1]. Since Wang and co-workers reported the photoactivity of polymeric graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ), many efforts have been made to investigate its environmental and energy applications, such as  $\text{H}_2$  evolution,  $\text{CO}_2$  reduction, pollutant degradation and  $\text{H}_2\text{O}_2$  production [2–8]. As a prospective organic semiconductor,  $g\text{-C}_3\text{N}_4$  possesses the characteristics of excellent thermal and chemical stability, cost effectiveness, easy preparation and relatively small bandgap (2.7 eV) for visible-light-driven photocatalysis [9]. For high-performance applications, various strategies, including morphology control, metal/non-metal

doping, co-catalyst deposition and creation of heterostructures, have also been developed to modify  $g\text{-C}_3\text{N}_4$  to improve its charge separation efficiency [10–18].

However, a fundamental understanding of the effect of carbon nitride microstructure on photocatalytic activity is still lacking. For example, several groups found that crystalline carbon nitride showed superior visible-light photoactivity toward hydrogen evolution [19,20]. In contrast, significantly enhanced activity of amorphous and less-crystalline carbon nitride has also been reported recently [21,22]. The presence of intrinsic structural defects has usually complicated this issue considerably. Based on previous reports, improved photocatalytic performance of carbon nitride can be achieved either through increasing structural defects (nitrogen or carbon vacancies) or decreasing  $\text{sp}^2$  nitrogen defects [23,24]. The discrepancies between these results largely depend on the diverse range of nitrogen-rich organic precursors that have been utilized for the preparation of carbon nitride through thermal polymerization. Thus, investigating the effect of the precursor

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on the microstructure and photoactivity is not only of scientific significance for a comprehensive understanding of carbon nitride architectures, but also technically important for the design of high-efficiency photocatalysts.

In addition to the strategy of material design, synergetic reaction is another promising way to improve photocatalytic efficiency. Generally, photo-induced electrons can contribute to photoreduction reactions, while separated holes play an important role in photooxidation reactions. The accelerated consumption of opposite-charge carriers undoubtedly results in the enhancement of overall efficiency [25,26]. A typical prototype for this is the widespread utilization of hole or electron scavengers during photocatalytic  $H_2$  or  $O_2$  evolution. Recently, this approach has also been demonstrated by selectively converting  $H_2S$  and  $O_2$  into  $S$  and  $H_2O_2$  [27]. The rational design of synergetic reactions during water treatment is also highly desirable, either for the efficient removal of environmental pollutants or simultaneous energy production. Thereafter, it is of great importance to develop high-efficiency carbon nitride as a metal-free photocatalyst for highly efficient synergetic applications [28].

Unfortunately, the relationship between carbon nitride microstructure and synergetic reactions remains largely unknown. It is of great importance to rationally design synergetic photocatalytic reactions and evaluate the effect of carbon nitride microstructure on the reaction applicability. 5-Sulfosalicylic acid (SSA) is an important chemical that is widely used in pharmaceutical production, metal plating, pigment manufacturing and leather tanning. Industrial wastewater including SSA can bring about severe environmental problems because of its substantial threats to human health. This issue is often complicated due to the coexistence of heavy metals, such as highly toxic hexavalent chromium  $Cr(VI)$ . The technical requirements for low-cost and efficient elimination of contaminants inspired us to investigate the great potential of metal-free carbon nitride for synergetic photocatalysis. Through coupling photooxidation of SSA with photoreduction of  $Cr(VI)$  or water, the removal of multiple contaminants or simultaneous hydrogen energy production can be reasonably expected.

In this study, metal-free  $g-C_3N_4$  photocatalysts with different microstructures were obtained through thermal polymerization of different nitrogen-containing organic precursors. The impact of carbon nitride microstructure on the synergetic photocatalytic performance and associated reaction pathways was comprehensively evaluated, using SSA degradation/ $Cr(VI)$  reduction and SSA degradation/hydrogen evolution as model reactions. Hydrogen bonds between polymeric melon strands contributed most to the efficiency of synergetic reactions, resulting in 3- and 8-fold improvements in contaminant removal and hydrogen production rates. It was also found that the successive formation of nitrogen vacancies and oxygen-doped structures were prerequisites for activating oxygen molecules, which provided new insights into defect engineering of carbon nitride for photocatalytic applications. Understanding the fundamental roles of hydrogen bonds and structural defects on the synergetic reaction mechanism could provide guiding principles for the design of high performance carbon nitride, as metal-free photocatalysts for environmental remediation.

## 2. Experimental section

### 2.1. Synthesis of $g-C_3N_4$

Different precursors purchased from J&K (Shanghai, China), including cyanamide, melamine and urea, were used to fabricate pure  $g-C_3N_4$  with different microstructures through a simple ther-

mal polycondensation method [29]. In a typical procedure, a certain amount of precursor powder was put into a crucible with a loose cover and heated in static air by a muffle furnace at  $550^\circ C$  for 4 h (heating rate:  $5^\circ C/min$ ). After cooling to room temperature, the yellow products were collected and ground into powders with a ceramic mortar for further use. For convenience of description, the products synthesized from urea, cyanamide and melamine are denoted as  $g-C_3N_4-U$ ,  $g-C_3N_4-C$  and  $g-C_3N_4-M$ , respectively.

### 2.2. Catalyst characterizations

The phase structure of carbon nitride was studied using a Bruker D8 Advance X-ray diffractometer (XRD). The morphology of products was observed using a Hitachi H-800 Transmission electron microscope (TEM). Fourier transform infrared spectra (FT-IR) were recorded on a Bruker Tenson 27 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic  $Al K\alpha$  radiation. UV–vis diffuse reflectance spectra (DRS) were collected by a UV-vis-NIR spectrometer (Varian, USA). Electron spin resonance (ESR) analysis was obtained using a Bruker electron paramagnetic resonance spectrometer (ESP 300E).

### 2.3. Evaluation of photocatalytic properties

Synergetic reactions were used to evaluate the photocatalytic activity of carbon nitride. For the simultaneous removal of organic pollutants and toxic  $Cr(VI)$ , 50 mg portions of photocatalysts were added into 100 mL deionized water solution with 10 mg/L  $Cr(VI)$  and 40 mg/L SSA, which were prepared using  $K_2CrO_4$  (>99%) and 5-Sulfosalicylic acid (>99%) purchased from Sinopharm Chemical Reagent Co., Ltd., (China). The pH was adjusted to 2 with 0.2 wt% HCl and 0.1 mol/L NaOH. Prior to irradiation, the suspension was ultrasonicated and magnetically stirred in the dark for 2 h to ensure uniform dispersion and adsorption/desorption equilibrium. Then, the suspension was irradiated by a 300 W Xe lamp. At given time intervals, 1.5 mL liquid samples were collected and filtered by microporous filtration membranes ( $0.45\ \mu m$ , PTFE) for chemical analysis. According to the 1,5-diphenylcarbazid photometric method (Chinese National Standard Procedure, GB7467-87), the concentration of  $Cr(VI)$  was determined by measuring the absorption of the pollutant solution at 540 nm, using a UV/Vis spectrophotometer (Hitachi, Japan). The SSA concentration was determined by a high-performance liquid chromatograph (HPLC) (Agilent, USA) [30]. The reduction or removal ratio of  $Cr(VI)$  and SSA were calculated by  $C/C_0$ , where  $C$  is the concentration of  $Cr(VI)$  or SSA at each irradiated time interval and  $C_0$  is the initial concentration of  $Cr(VI)$  or SSA.

The potential application of a synergetic strategy for simultaneous removal of organic pollutants and hydrogen energy production was also investigated. Photocatalytic  $H_2$  evolution was conducted in a Pyrex reaction vessel connected to a glass-closed-gas circulation system [31,32]. For each reaction, 50 mg of carbon nitride was dispersed and sonicated for 20 min in 100 mL aqueous solution. The concentration of SSA contaminant was 50 mg/L.  $H_2PtCl_6$  dissolved in the reactant solution was used to photodeposit 3 wt% of Pt co-catalyst onto the carbon nitride. Then the reactor was sealed and evacuated several times to remove air before being irradiated under a 300 W Xe lamp. The temperature of the reaction solution was carefully controlled to about  $5^\circ C$  throughout the experiments. The amount of evolved  $H_2$  was analyzed by gas chromatography (GC-7900) with argon as carrier gas.

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