



## Research Paper

Amorphous NiO as co-catalyst for enhanced visible-light-driven hydrogen generation over g-C<sub>3</sub>N<sub>4</sub> photocatalystJianni Liu<sup>a,b</sup>, Qiaohui Jia<sup>a</sup>, Jinlin Long<sup>b</sup>, Xuxu Wang<sup>b</sup>, Ziwei Gao<sup>a,\*</sup>, Quan Gu<sup>a,b,\*</sup><sup>a</sup> Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, PR China<sup>b</sup> State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, 350002, PR China

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## ABSTRACT

This study was mainly aimed at constructing an amorphous NiO modified g-C<sub>3</sub>N<sub>4</sub> non-noble metal heterojunction photocatalyst for enhanced visible-light hydrogen evolution. The Ni species modified g-C<sub>3</sub>N<sub>4</sub> sample was firstly prepared through the wetness impregnation method and then the phase and crystallinity of Ni species co-catalysts on g-C<sub>3</sub>N<sub>4</sub> were adjusted by the thermal oxidation at different temperature. The detailed characterizations revealed that the amorphous NiO co-catalysts are supported successfully on g-C<sub>3</sub>N<sub>4</sub>, and the C–O–Ni linkages in the amorphous NiO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions are formed at NiO and g-C<sub>3</sub>N<sub>4</sub> interface after annealing at 300 °C. Compared to bare g-C<sub>3</sub>N<sub>4</sub> and crystalline NiO modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts, amorphous NiO modified g-C<sub>3</sub>N<sub>4</sub> non-noble metal photocatalyst showed significantly enhanced visible-light photocatalytic hydrogen production activity. The amorphous NiO co-catalysts provided more active sites for H<sub>2</sub> evolution and amorphous NiO modification caused the enhanced visible-light response. Moreover, amorphous NiO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions formed at interface between amorphous NiO and host g-C<sub>3</sub>N<sub>4</sub> created an inner electric field, which allowed for the transfer of the photogenerated electrons of g-C<sub>3</sub>N<sub>4</sub> across the interfacial C–O–Ni linkages to amorphous NiO co-catalysts and thus significantly promoted the migration and separation of photogenerated charge carriers.

## 1. Introduction

Metal free g-C<sub>3</sub>N<sub>4</sub> polymer material composed of nature abundant elements (C and N) has been regarded as a promising material for photocatalytic H<sub>2</sub> evolution because it is non-toxic, low cost, high stability and has excellent optical properties and electronic structure [1–11]. However, the bare g-C<sub>3</sub>N<sub>4</sub> material hardly showed the photocatalytic activity for H<sub>2</sub> evolution under visible-light irradiation due to the low separation efficiency and high recombination of photo-generated charge carriers, the high surface overpotential for hydrogen release as well as the lack of surface active sites for H<sub>2</sub> evolution. Generally, the noble metal co-catalysts [1,12–16], such as Pt nanoparticles, are loaded on g-C<sub>3</sub>N<sub>4</sub> surface to enhance charge transfer and provide active sites for the H<sup>+</sup> reduction and finally to realize photocatalytic hydrogen production over g-C<sub>3</sub>N<sub>4</sub>. The introduction of noble metal co-catalysts, however, increases the cost of the photocatalyst, which will greatly limit its practical applications.

Therefore, it is of great importance to develop earth-abundant and low-cost hydrogen evolution co-catalysts as alternatives. Fe, Co, Ni, Cu,

Zn, and carbon based materials (iron (III) porphyrin, CoS, Ni(OH)<sub>2</sub>, NiS, Cu<sub>2</sub>O, ZnIn<sub>2</sub>S<sub>4</sub>, carbon QDs and so on) [8,17–22] have been intensively studied as effective co-catalysts for this purpose. For example, the rate of H<sub>2</sub> evolution over g-C<sub>3</sub>N<sub>4</sub> under visible-light illumination was significantly improved after loading with CoS [18]. Yu et al. [19] reported that utilization of low-cost Ni(OH)<sub>2</sub> as a substitute for noble metals (such as Pt) in the photocatalytic H<sub>2</sub> production for g-C<sub>3</sub>N<sub>4</sub>. Liu et al. [21] demonstrated that core@shell Cu<sub>2</sub>O@g-C<sub>3</sub>N<sub>4</sub> shows efficient visible-light photocatalytic hydrogen evolution and enhanced photostability. However, it was found that the non-noble metal promoters are less effective in improving photocatalytic efficiency compared to noble metal catalysts such as Pt.

It has been also revealed that the photocatalytic activity of co-catalysts modified samples strongly depends on the crystal structure, morphology, especially crystallinity and particle size of co-catalyst. In the research of microstructure of co-catalysts, many of discoveries and breakthroughs have been reported, ranging from crystal to amorphous structure, clusters, even to single atom or single site. For example, Kong et al. [23] developed a novel amorphous CoSn<sub>x</sub>O<sub>y</sub> decorated graphene

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nanohybrid photocatalyst, which shows efficient photocatalytic hydrogen evolution. Yuan et al. [24] demonstrated that H<sub>2</sub> evolution activity of CdS is significantly enhanced in the presence of the amorphous Co<sub>3</sub>O<sub>4</sub> co-catalyst. Liu et al. [25] grafted Cu(II) oxide amorphous nanoclusters on Ti<sup>3+</sup> self-doped TiO<sub>2</sub> to improve the visible-light photocatalytic activity. Chen et al. [26] prepared the amorphous NiO modified N/TiO<sub>2</sub> for visible-light photocatalytic hydrogen evolution. They believed that the molecular Ti–O–Ni heterojunctions promote the transfer and separation of photogenerated electrons and holes. Also, Fan et al. [27] reported single-site nickel-grafted anatase TiO<sub>2</sub> for hydrogen production and revealed that the Ti–O–Ni *p-n* heterojunctions create visible light absorption and photocatalysis. Li et al. [28] found that loading isolated single Pt atoms as co-catalyst on g-C<sub>3</sub>N<sub>4</sub> significantly enhances the photocatalytic activity for H<sub>2</sub> evolution. Amorphous structure and clusters (even single atom and single site species), generally, have much smaller bandgap, lack the long-range atomic order and have many defects, which allow for harvesting visible light, promoting charge transfer and providing more active sites for photocatalytic reaction.

Herein, in the present work, we aimed to constructing an amorphous NiO modified g-C<sub>3</sub>N<sub>4</sub> non-noble metal heterojunction photocatalyst for enhanced visible-light hydrogen evolution. The Ni species modified g-C<sub>3</sub>N<sub>4</sub> sample was annealing at different temperature to control the phase and crystallinity of Ni species co-catalysts on g-C<sub>3</sub>N<sub>4</sub>. After annealing at 300 °C, the amorphous NiO co-catalysts were formed on g-C<sub>3</sub>N<sub>4</sub>, and the C–O–Ni linkages in the amorphous NiO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions were formed at NiO and g-C<sub>3</sub>N<sub>4</sub> interface. For comparison, two kind of crystalline NiO modified g-C<sub>3</sub>N<sub>4</sub> samples (Ni/g-C<sub>3</sub>N<sub>4</sub>-CI and Ni/g-C<sub>3</sub>N<sub>4</sub>-CH) were prepared by the hydrothermal method and the impregnation method as control samples. Photocatalytic activity results showed that amorphous NiO modified g-C<sub>3</sub>N<sub>4</sub> photocatalyst has significantly enhanced visible-light photocatalytic hydrogen production activity as compared to bare g-C<sub>3</sub>N<sub>4</sub> and crystalline NiO modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts. The results of photocatalytic activity and characterization indicated that the amorphous NiO co-catalysts have great roles in photocatalytic H<sub>2</sub> evolution over g-C<sub>3</sub>N<sub>4</sub>. First, the amorphous NiO co-catalysts provided more active sites for H<sub>2</sub> evolution. Second, amorphous NiO modification caused the enhanced visible light response. Last, amorphous NiO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions allowed for the transfer of the photogenerated electrons of g-C<sub>3</sub>N<sub>4</sub> across the interfacial C–O–Ni linkages to amorphous NiO co-catalysts and thus significantly promoted the migration and separation of photogenerated charge carriers.

## 2. Experimental section

### 2.1. Preparation of g-C<sub>3</sub>N<sub>4</sub>

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was prepared by thermal polycondensation using melamine and ammonia chloride as precursors according to the reported reference [29]. Typically, 4 g melamine and 10 g ammonia chloride was mixed and ground in a mortar. The mixture was put in a crucible with cover and annealed at 550 °C for 4 h with a heating rate of 4 °C min<sup>-1</sup> in a muffle furnace.

### 2.2. Preparation of Ni(OH)<sub>2</sub> modified g-C<sub>3</sub>N<sub>4</sub>

Ni(OH)<sub>2</sub> modified g-C<sub>3</sub>N<sub>4</sub> was prepared via a facile impregnation method. In a typical process, 1.0 g of g-C<sub>3</sub>N<sub>4</sub> powders were dispersed in 50 mL water with continuous stirring in a beaker. Thereafter, a desired amount of nickel chloride solution (20 mg/mL) was added in above suspension under vigorous stirring and then the pH of solution was adjusted to 12.0 using 28.0% ammonia. After stirring overnight, the suspension was dried in the oven.

### 2.3. Preparation of Ni/g-C<sub>3</sub>N<sub>4</sub>

Amorphous NiO modified g-C<sub>3</sub>N<sub>4</sub> (denoted as Ni/g-C<sub>3</sub>N<sub>4</sub>) was prepared via post annealing of Ni(OH)<sub>2</sub> modified g-C<sub>3</sub>N<sub>4</sub>. The obtained Ni(OH)<sub>2</sub> modified g-C<sub>3</sub>N<sub>4</sub> was annealed at different temperature (100 °C, 200 °C, 300 °C, 400 °C, and 500 °C) for 3 h in air and the final products were ground in a mortar to get photocatalysts (denoted as Ni/g-C<sub>3</sub>N<sub>4</sub>-T, T refers to the annealing temperature: 100, 200, 300, 400, and 500). For the preparation of Ni<sub>x</sub>/g-C<sub>3</sub>N<sub>4</sub> with different NiO contents (x = 0.5, 1.0, 3.0, 5.0, 7.0, 9.0, 10, represents NiO content, NiO wt.% = 0.5%, 1.0%, 3.0%, 5.0%, 7.0%, 9.0%, 10%), added amount of nickel chloride solution (20 mg/mL) is 0.8, 1.6, 4.9, 8.4, 12.0, 15.8, 17.7 mL, respectively.

### 2.4. Preparation of Ni/g-C<sub>3</sub>N<sub>4</sub>-C

For comparison, two kinds of crystalline NiO modified g-C<sub>3</sub>N<sub>4</sub> (denoted as Ni/g-C<sub>3</sub>N<sub>4</sub>-C) was prepared via different treatment process as follows: (1) the sample denoted as Ni/g-C<sub>3</sub>N<sub>4</sub>-CI was prepared via an impregnation method and post heat treatment. Firstly, a desired amount of nickel chloride solution (20 mg/mL) was added in 50 mL water under vigorous stirring in a beaker and then the pH of solution was adjusted to 12.0 using 28% ammonia. 0.8, 1.6, 4.9, 8.4, 12.0, 15.8, 17.7 mL nickel chloride solution was used for the preparation of Ni<sub>x</sub>/g-C<sub>3</sub>N<sub>4</sub>-CI with different NiO contents, where x represent NiO content, NiO wt% = 1.0%, 3.0%, 5.0%, 7.0%, 9.0%, 10%, respectively. Thereafter, 1.0 g of g-C<sub>3</sub>N<sub>4</sub> powders were dispersed in above solution with vigorous stirring for 30 min and the powder product was collected via centrifugation, washed with distilled water and ethanol, respectively, and dried at 60 °C in an oven. The final product was obtained after annealing at 300 °C for 3 h in air. (2) the sample denoted as Ni/g-C<sub>3</sub>N<sub>4</sub>-CH was prepared by a hydrothermal method and post heat treatment. Typically, 1.0 g of g-C<sub>3</sub>N<sub>4</sub> powders, 50 mL water, and a desired amount of nickel chloride solution (20 mg/mL) were added in turn into a 100 mL beaker. The pH of solution was adjusted to 10.0 using 28% ammonia with continuous and vigorous stirring for 30 min. Then the solution was put into a 100 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 160 °C for 6 h. After reaction, the powder product was collected via centrifugation, washed with distilled water and ethanol, respectively, and dried at 60 °C in an oven. The final product was obtained after heat treatment at 300 °C for 3 h in air.

### 2.5. Characterizations

The X-ray Diffraction (XRD) patterns of all samples were collected on Rigaku D/Max2550VB+/PC (Cu Kα source) at a scan rate of 2.4° min<sup>-1</sup>. Transmission Electron Microscopy (TEM) images and element mapping were obtained by a Tecnai G2 F20 transmission electron microscopy (FEI, USA) at an accelerating voltage of 200 kV. UV–vis Diffuse Reflectance Spectrum (UV–vis DRS) was measured by a UV/vis spectrophotometer (UV-Lambda 950, Perkin Elmer). Fourier Transform Infrared spectra (FTIR) were derived from Perkin Elmer Fourier Transform Infrared Spectrometer GX. Photoluminescence (PL) spectra were accomplished in solid with Shimadzu RF5301 Spectrofluorophotometer with an excitation wavelength of 380 nm. X-ray Photoelectron Spectroscopy (XPS) spectra were determined on a VG ESCALAB 250 XPS system with a monochromatized Al Kα X-ray source (15 kV, 200 W). Nitrogen adsorption-desorption isotherms were performed at 77 K using Micromeritics ASAP 2010 equipment.

### 2.6. Photocatalytic H<sub>2</sub> generation

The photocatalytic activities for hydrogen evolution under visible light, UV light, or solar light irradiation were performed in a closed gas-recirculation system equipped with a top-irradiation Pyrex reaction

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