



Porous carbon nitride with defect mediated interfacial oxidation for improving visible light photocatalytic hydrogen evolution

Zhao Zhang^a, Luhua Lu^{a,b,*}, Zaozao Lv^a, Ying Chen^{a,b}, Hongyun Jin^a, Shuen Hou^a, Lixin Qiu^c, Limei Duan^c, Jinghai Liu^{c,**}, Kai Dai^d

^a Faculty of Materials Science and Chemistry, China University of Geosciences Wuhan, 388 Lumo Road, Wuhan 430074, PR China

^b Zhejiang Institute, China University of Geosciences Wuhan, Hangzhou, 311305, PR China

^c Inner Mongolia Key Laboratory of Carbon Nanomaterials, College of Chemistry and Chemical Engineering, Inner Mongolia University for Nationalities, Tongliao, 028000, PR China

^d College of Physics and Electronic Information, Huaibei Normal University, Huaibei, 235000, PR China

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ABSTRACT

The Feasibility of interfacial redox reaction has determinant role in hydrogen evolution during photocatalytic water-splitting process. Here, we report that promoting interfacial oxidation ability of porous graphitic carbon nitride (Pg-C₃N₄) with defects can effectively improve visible light photocatalytic hydrogen evolution (PHE) activity. Pg-C₃N₄ with edge site defects was fabricated by constraining growth of g-C₃N₄ on porous kaolinite-derived template. The Pg-C₃N₄ with extra electrons of defects caused by enriched basal plane holes exhibits higher electrocatalytic activity for oxidation process in comparison with reduction process. This feature benefits electron-transfer reaction to quench photo-excited holes during photocatalysis process and promote photo-electrons reaction, which was proved by photoluminescence spectra of Pg-C₃N₄ and g-C₃N₄ and different PHE activity variation of their heterojunction materials with TiO₂. The results show that PHE rate for Pg-C₃N₄ reaches 1917 $\mu\text{mol}^{-1} \text{g}^{-1} \text{h}^{-1}$, 2.37 times of g-C₃N₄ under visible light irradiation. This approach of engineering interfacial defects to accelerate hole's oxidation reactions during photocatalytic water-splitting would advance two-dimensional (2D) catalysis for solar fuel production.

1. Introduction

Photocatalytic hydrogen evolution (PHE) by water-splitting half-reaction with semiconductor photocatalysts has been recognized as a clean energy production approach [1]. To produce hydrogen via photocatalytic approach, sufficient conduction band potential (CBP) of semiconductor materials is needed to provide overpotential for hydrogen evolution. Graphitic carbon nitride (g-C₃N₄) with CBP at -1.24 V with respect to normal hydrogen electrode potential (NHE) and narrow band-gap has been employed as a metal-free photocatalyst for water-splitting to H₂ under visible light irradiation [2,3]. The chemical inert character of g-C₃N₄ endows it with stable cyclic photocatalytic performance. However, photocatalytic activity of g-C₃N₄ under visible light is very low in comparison to other semiconductor nanomaterials such as metal oxides [4,5], metal oxynitrides [6], and metal sulphides [7]. It is considered that the structural defects of g-C₃N₄ would localize photo-generated polarons and accelerate their recombination, which prohibits the production and transfer of interfacial

free electrons to produce hydrogen. Guided by this idea, intensive researches [8–16] have thus been done to increase visible light absorption by narrowing the band-gap, to improve charge separation by constructing heterojunctions, increase surface hydrogen evolution sites by increasing specific surface area (SSA) and introduce cocatalyst such as Pt [17], AuPd [18], WS₂ [19], MoS₂ [20], CoS [21], NiP [22] and Ni/NiO [23].

Generally, PHE reaction involves three major steps: (i) light absorption by semiconductor photocatalysts to generate electron-hole pairs, (ii) charge separation and migration to surface active sites, (iii) interfacial reactions for reduction of protons to H₂ and oxidation of OH⁻ (for full water splitting) or sacrificial electron donors (for half-reaction). The first two steps are related to fast photoelectrical process along with the third step of electrochemical process. During this electrochemical reaction process, both reduction reaction (electrons reactions) and oxidation reaction (holes reactions) are spontaneous process on the interface and the slow one is considered as the rate-determined step with large overpotential. Therefore, tremendous attentions have

* Corresponding author at: Faculty of Materials Science and Chemistry, China University of Geosciences Wuhan, 388 Lumo Road, Wuhan 430074, PR China.

** Corresponding author.

E-mail addresses: lhlu@cug.edu.cn (L. Lu), jhliu2015@imun.edu.cn (J. Liu).

been paid on exploring hydrogen evolution active sites provided by cocatalysts such as platinum (Pt), which serves as an electron sink with suitable hydrogen absorption free energy [17]. However, protons reduction by electrons would be suppressed if holes reaction on the interface is slow [24]. To well understand PHE process on the g-C₃N₄, it is necessary to investigate the interfacial hole reaction activity. Recently, research has shown that addition of K₂HPO₄ facilitates hole oxidation kinetics that dramatically improve hydrogen evolution activity on g-C₃N₄ nanosheets [25]. Besides, decorating hole reaction cocatalyst CoP on Pt-g-C₃N₄ further increase hydrogen evolution due to the increased oxygen evolution rate [26]. Although these research have achieved important progress, little attentions have been focus on investigating the effects of intrinsic structure of g-C₃N₄ on hole reaction kinetics during PHE process.

Herein, we report a defect rich porous g-C₃N₄ (Pg-C₃N₄) obtained by confined pyrolysis of urea on porous hard template obtained by modification of natural nanomaterial kaolinite. Pg-C₃N₄ with rich edge site defects have shown obviously enhanced PHE activity under visible light irradiation. Electrochemical analysis has shown that interfacial oxidation activity of Pg-C₃N₄ is much higher than that of g-C₃N₄, while keeping the same interfacial reaction activity towards protons reduction. Interfacial junction construction along with photocurrent analysis also demonstrate that defects on Pg-C₃N₄ present excellent capability to mediate hole reaction towards interfacial oxidation and photocurrent increase.

2. Experimental

2.1. Preparation

To prepare porous hard template, 50 g kaolinite powder was annealed at 850 °C in air atmosphere for 2 h to transfer it into amorphous metal kaolinite. Then annealed powder was stirred in 300 mL 2 M HCl overnight twice followed by washing with 2 L deionized water and drying at 80 °C to remove Al₂O₃ phase obtaining a porous product composed of amorphous SiO₂. Then, 10 g urea (AR, Sinopharm Chemical Reagent Co., Ltd) was mixed with 20 g porous template and placed in a covered corundum crucible and heated to 550 °C with temperature increase rate of 10 °C/min and preserved for 3 h in air atmosphere and naturally cooled to room temperature in a tube furnace. Then, the sample was washed with 100 mL HF (10%) three times at 60 °C 100 mL nitric acid (0.1 mol L⁻¹) and 1 L distilled water (DI water) to remove SiO₂ and other impurities followed by filtering and drying at 80 °C to obtain Pg-C₃N₄. g-C₃N₄ was synthesized without template in the same thermal treatment program without HF washing. Pt loaded Pg-C₃N₄ (or g-C₃N₄) was obtained by photodeposition. 0.3 mL H₂PtCl₆ · 6H₂O (10 mg mL⁻¹, AR, Sinopharm Chemical Reagent Co., Ltd) and 2 mL acetic acid (1 mol L⁻¹, Sinopharm Chemical Reagent Co., Ltd) were added into 100 mL g-C₃N₄ dispersion (1 mg mL⁻¹) to obtain 3 wt% Pt-g-C₃N₄ (or Pt-Pg-C₃N₄). After N₂ bubbling for an hour to remove the oxygen (O₂) in the system, the sample was irradiated by a 300 W Xe lamp (PLS-SXE 300, Beijing Perfect light Technology Co., Ltd) for three hours. Then, the Pt-g-C₃N₄ (or Pt-Pg-C₃N₄) was obtained by filtering and drying at 80 °C overnight. For preparation of Pt-g-C₃N₄-TiO₂ and Pt-Pg-C₃N₄-TiO₂, the above prepared sample were bath sonicated with TiO₂ (Degussa P25) at mass ratio of 1:9 of TiO₂ to g-C₃N₄ or Pg-C₃N₄ for 1 h in 100 mL deionized water followed by filtration and drying at 80 °C overnight.

2.2. Characterization

All measurement was carried out in 25 °C room temperature environment. Morphology of samples was characterized through TEM (Tecnai G2 F20S-TWIN at 200 kV). Structure analysis was carried out through XRD (Bruker AXS D8-Focus) BET (Micromeritics ASAP2020) and XPS (X'Pert-Pro MPD using Cu Kα (λ = 1.5406 Å)). UV-vis DRS

measurements were carried out using a Hitachi UV-3600 UV-vis spectrophotometer equipped with an integrating sphere attachment. Analysis range was from 200 to 600 nm, and BaSO₄ was used as a reflectance standard. PL spectra of photocatalysts were measured by FLS920 with excitation wavelength of 325 nm. The EPR spectra were obtained on a JES-FA 200 EPR spectrometer.

2.3. Hydrogen (H₂) evolution test

Photocatalytic water splitting reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. 80 mg Pt loaded catalyst was dispersed in a mixture of 54 mL deionized water and 6 mL triethanolamine (TEOA) (78%, Sinopharm Chemical Reagent Co., Ltd) by sonication for 0.5 h. The obtained reactant dispersion was put into reaction vessel and stirred. Reaction system was evacuated three times with half an hour each time to remove air completely prior to irradiation under a 300 W Xe lamp with water filter. Wavelength of incident light was controlled by using cut-off filters (> 400 nm). The temperature of reactant solution was maintained at room temperature by a flow of cooling water during reaction. Evolved gases were analyzed by gas chromatography (GC 7890II, Shanghai Techcomp Instrument Ltd.) equipped with a thermal conductive detector (TCD) with argon as carrier gas.

2.4. Electrochemical measurements

Electrochemical measurements were carried out on a CHI760E electrochemical work station (Shanghai Chenhua) in three electrodes system. To remove bubbles generated during measurement, rotation speed of electrode has been controlled 1600 rpm by MRS electrode rotator (Pine Research Instrumentation, USA). Typically, 1 mg of catalyst and 10 μl of 5 wt% Nafion solution were dispersed in 1 ml of 6:1(v/v) water/ethanol and sonication for 2 h to form a homogenous solution. 60 μl solution was loaded on a 5-mm-diameter clean glassy carbon rotation disk electrode (mass loading 0.306 mg cm⁻²) and dried under room temperature. Measurement was carried out in 10% TEOA solution that was used for PHE test, with a Pt wire as counter electrode and reference electrode was Ag/AgCl. LSV measurement was scanned at scan rate of 2 mV s⁻¹. Before measurement, electrolyte solution was bubbled with N₂ and H₂ for 1 h to completely remove O₂ and scanned CV from -1 V to 2 V until a stable curve is achieved.

3. Results and discussion

Synthetic process of Pg-C₃N₄ can be seen in Fig. 1A. The detailed structure variation from raw kaolinite to porous template via thermal annealing and acid washing can be seen in supporting information (See Fig. S1). Pyrolysis of urea on porous template has resulted in uniform deposition of g-C₃N₄ on template surface as has been confirmed via TEM imaging (Fig. 1B and C) and element mapping of C, N, O and Si (Fig. 1D, E, F and G). By removing amorphous phase of SiO₂ via HF washing, Pg-C₃N₄ was obtained. Pg-C₃N₄ has shown large amount of in-plane holes (Fig. 1H). For comparison, g-C₃N₄ (Fig. 1I) synthesized without template has shown no in-plane holes. In accordance with porous structure confirmed by TEM analysis, N₂ adsorption/desorption isotherm curves in Fig. 1J has shown that Pg-C₃N₄ has BET specific surface area of 109 m²/g, which is much higher than 40 m²/g of g-C₃N₄. The pore volume distribution of Pg-C₃N₄ and g-C₃N₄ in Fig. 1K has shown increased pore volume of Pg-C₃N₄ over g-C₃N₄ from 2 to 61 nm pore size range. Moreover, a peak at 2.14 nm pore size of Pg-C₃N₄ was found indicating the porous hard template directed synthesis of Pg-C₃N₄ has led to smaller pore formation in compared with that of g-C₃N₄ synthesized without template. Thus, template directed synthetic approach of Pg-C₃N₄ endow it large specific surface area along with rich-pore formation.

The structure of Pg-C₃N₄ was probed by X-ray Diffraction (XRD) and

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