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Interlayer interaction in ultrathin nanosheets of graphitic carbon nitride for efficient photocatalytic hydrogen evolution



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Daming Zhao^{a,1}, Jie Chen^{a,1}, Chung-Li Dong^b, Wu Zhou^a, Yu-Cheng Huang^{b,c}, Samuel S. Mao^{d,e}, Liejin Guo^a, Shaohua Shen^{a,f,*}

^a International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China ^b Department of Physics, Tamkang University, 151 Yingzhuan Road, New Taipei City 25137, Taiwan

^c Department of Electrophysics, National Chiao Tung University, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan

^d Samuel Mao Institute of New Energy, Science Hall, 1003 Shangbu Road, Shenzhen 518031, China

^e Department of Mechanical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

^fXi'an Jiaotong University Suzhou Academy, Suzhou 215123, China

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ABSTRACT

Two-dimensional graphitic carbon nitride $(g-C_3N_4)$ nanosheets (CNNS) have attracted intense interest in photocatalysis, given their small thickness and high specific surface area favoring charge transfer and surface reactions. Herein, a facile strategy of breaking and following repolymerizing the heptazine units in bulk g-C_3N_4 (BCN) is developed to synthesize ultrathin CNNS with thickness of 1 nm in relatively high product yield (~24%). The as-prepared 1 nm-thick CNNS show significantly enhanced photocatalytic performance for hydrogen evolution than BCN and even the 3 nm-thick CNNS acquired by thermal oxidation etching of BCN. It is evidenced that the disordered layer structure of the obtained ultrathin CNNS causes strong interlayer C–N interaction, tunneling electron transport between the C–N layers. Meanwhile, the broken in-plane C–N bonds create more unsaturated N sites in the 1 nm-thick CNNS, facilitating the electron excitation from the occupied states in g-C_3N_4 to its unoccupied states for water reduction reaction. © 2017 Elsevier Inc. All rights reserved.

1. Introduction

Photocatalytic solar hydrogen conversion has attracted extensive attention as a feasible solution to energy shortage and environmental pollution [1,2]. To search for photocatalytic materials with high activity as well as good stability, a myriad of semiconductor photocatalysts, including oxides, sulfides, and nitrides, have been developed in the past decades [3,4]. Metal-free graphitic carbon nitride (g-C₃N₄) has emerged as a promising visible-light-driven photocatalyst for solar hydrogen production owing to its earth-abundance, environmental friendliness, chemical stability, and proper band positions for water redox reactions [5–10]. Unfortunately, the photocatalytic efficiency of bulk g-C₃N₄ (BCN) is still far from satisfaction, largely due to its low specific surface area and high recombination rate of photogenerated electron-hole pairs [11–16]. To conquer these limitations and thus improve the photo-

¹ These authors contributed equally to this work.

catalytic activity of g-C₃N₄, great efforts have been made from the viewpoint of chemical structure adjustment and nanostructure design. Important examples include doping with heteroatoms [17–20], compositing with other semiconductors [21–24], copolymerizing with organic molecules [25,26], and morphology design [27–32], *etc.* All these efforts have rendered great enhancement in the photocatalytic activity for hydrogen evolution over g-C₃N₄.

g-C₃N₄ has a layered structure, with tri-s-triazine (heptazine) units composed of carbon and nitrogen elements in each layer and weak van der Waals force between the layers [32]. With inspiration from the seminal discovery of graphene [33], reducing the dimensionality of BCN into two-dimensional (2D) g-C₃N₄ nanosheets (CNNS) has been proved an effective strategy to exploit the potential of g-C₃N₄ for photocatalytic hydrogen generation, by optimizing its physicochemical properties, such as decreasing thickness, increasing specific surface area, and enhancing charge carrier mobility [32,34–36]. Up to now, CNNS have been successfully prepared by thermal etching [32,35,36] and liquid ultrasonic exfoliation [34] from BCN *via* breaking the van der Waals forces between the layers. In these studies, CNNS with thickness of 2– 3 nm were obtained, and without exception exhibited much higher photocatalytic activities for hydrogen evolution than BCN. Such

^{*} Corresponding author at: International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China.

E-mail address: shshen_xjtu@mail.xjtu.edu.cn (S. Shen).

photocatalytic enhancement could be attributed to the small thickness of CNNS, rendering promoted charge transfer and separation. However, these CNNS with thickness of 2–3 nm still contain 6–9 C–N atomic layers (theoretical value of monolayer g-C₃N₄ is 0.33 nm [36]), which led to confined charge transport in CNNS, limiting the further improvement of photocatalytic activity. It could be thus expected that the CNNS with smaller thickness, namely, less atomic layers, could exhibit more efficient photocatalytic hydrogen evolution. Recently, some chemical exfoliation strategies have been developed to synthesize ultrathin and even monolayer CNNS, which achieved significantly enhanced photocatalytic performance for hydrogen evolution as expected [31,37,38]. However, these developed chemical methods are still facing problems of long time and/or multiple-step synthesis procedure as well as relatively low product yields (<10%). Thus, it is still essential to develop a facile, rapid and scalable method to synthesize ultrathin CNNS with high photocatalytic activities.

Herein, by breaking and then repolymerizing the heptazine units in BCN, we propose a two-step ultrasonication-calcination method to prepare ultrathin CNNS with thickness of only 1 nm (3 atomic layers) in relatively high product yield (~24%). Remarkably, with the unique disordered layer structure for interlayer tunneled charge transport and broken in-plane C—N bonds in CNNS for efficient electron excitation, the resultant 1 nm-thick ultrathin CNNS exhibit excellent activity and stability for photocatalytic hydrogen evolution under visible light.

2. Experimental

2.1. Synthesis of bulk $g-C_3N_4$

All chemicals in the present study are of analytical grade and used as received without further purification. Deionized water was used throughout the experiments. Bulk g-C₃N₄ (BCN) was synthesized by the well reported thermal polymerization method [39]. Typically, 2 g of melamine was put into an alumina crucible with a cover, and calcined at 520 °C in air for 4 h with a ramping rate of 5 °C/min.

2.2. Synthesis of $g-C_3N_4$ nanosheets

The ultrathin $g-C_3N_4$ nanosheets (denoted as CN-UC, where U means ultrasonication and C means calcination) were synthesized by an ultrasonication-calcination two-step process. In detail, 0.5 g of as-prepared BCN was added into 200 mL of deionized water in a 250 mL glass beaker. After high-powered ultrasonication treatment (900 watts) under stirring for 2 h, the obtained product was centrifugalized and dried in air at 80 °C for 8 h. The resultant powder, denoted as CN-U, was collected and calcined at 520 °C in air for 4 h with a ramping rate of 5 °C/min. Then the light yellow powder of CN-UC was obtained. The quantity of as-prepared CN-UC was approximately 0.12 g, which corresponds to a high product yield of 24%. The reference sample of CN-C was acquired by a direct calcination of BCN using the same temperature.

2.3. Characterization

Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 F30 S-Twin transmission electron microscope at an accelerating voltage of 300 kV. Atomic force microscopy (AFM) images were obtained from a NT-MDT Solver Next atomic force microscope. X-ray diffraction (XRD) patterns were collected on a PANalytical X'pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu K α irradiation (Wavelength = 1.5406 Å). Fourier transform infrared (FTIR) spectra were recorded on a

Bruker Vextex 70 FTIR spectrometer using the KBr pellet technique. The synchrotron X-ray spectroscopic (XAS) measurements at C and N K-edge were performed at BL20A, at the National Synchrotron Radiation Research Center, Taiwan. Solid-state ¹H crosspolarisation magic angle spinning nuclear magnetic resonance (CP-MAS-NMR) spectra were recorded by a Bruker Avance 400 spectrometer operating at 12 KHz resonance frequency. X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos Axis-Ultra DLD instrument with a monochromatized Al Ka line source (150 W). All the binding energies were referenced to the C 1 s peak at 284.8 eV. The steady-state photoluminescence (PL) emission spectra and time-resolved transient PL decay spectra were carried out at room temperature using a PTI QM-4 fluorescence spectrophotometer. The charge decay kinetics calculation methods were depicted in Supplementary material (Decay kinetics calculation methods). Electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMX X-band spectrometer and microwave frequency = 9.40 GHz at room temperature. N_2 adsorption-desorption isotherms were conducted at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020, Micromeritics) after degassing the samples at 150 °C for 4 h. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) methods. UV-vis diffuse reflectance spectra were recorded on a Cary Series UV-vis-NIR spectrophotometer (Agilent Technologies).

2.4. Photocatalytic measurements

Photocatalytic hydrogen evolution reactions were performed in a 230-mL gas-closed Pyrex reactor. In a typical photocatalytic reaction, 50 mg photocatalysts were dispersed in 200 mL aqueous solution of triethanolamine (TEOA, 10 vol%) by a magnetic stirrer with constant rotational velocity. 1 wt% Pt as cocatalyst was in situ photodeposited on the photocatalyst from the precursor of H₂PtCl₆-6H₂O. Nitrogen was purged through the reactor for 20 min before reaction to remove the residual air. A 300 W Xe lamp with a 420 nm cutoff filter was used to trigger the photocatalytic hydrogen generation. The temperature of the reaction solution was kept at 35 °C via a circulating water pump during the whole experiment. Evolved hydrogen was measured through a thermal conductivity detector (TCD) gas chromatograph (NaX zeolite column, nitrogen as the carrier gas). Blank experiments revealed no appreciable hydrogen evolution without irradiation or photocatalysts. The measurement and calculation of apparent quantum yield (AQY) and turnover number (TON) was depicted in details in Supplementary material.

3. Results and discussion

Starting from BCN prepared by thermal polymerization of melamine [39], ultrathin CNNS were successfully obtained via an ultrasonication-calcination two-step process (see Experimental Section for details and Fig. S1 for preparation process in Supplementary material). As shown in Fig. 1, the as-prepared BCN, aggregated as large thick sheets (Fig. 1a), was shattered and broken into small and thin pieces (Fig. 1b) through the first ultrasonication step (denoted as CN-U, U means ultrasonication). Interestingly, the following calcination step then induced the repolymerization of small CN-U pieces into ultrathin CNNS (denoted as CN-UC, where U and C means ultrasonication and calcination, respectively) with thickness of only 1 nm (3 atomic layers) (Fig. 1c and d). In comparison, much thicker CNNS were obtained via a thermal oxidation exfoliation process by calcination of BCN in air (denoted as CN-C), which has larger thickness of 3 nm (9 atomic layers) (Fig. 1e and f), agreeing well with the previous study [32]. Moreover, CN-UC was Download English Version:

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