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Rational synthesis of ultrathin graphitic carbon nitride nanosheets for efficient photocatalytic hydrogen evolution

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) nanosheets with unique structural and electronic properties have received much attention in photocatalysis, yet the direct synthesis of ultrathin g-C_3N_4 is still a big challenge. Herein, high-performance g-C_3N_4 nanosheets were firstly prepared by directly thermal calcination of the hydrothermally pretreated melamine as precursor. Multiple techniques were carried out to characterize the as-prepared samples. Results shown that the morphologies, microstructures, and physicochemical properties of as-synthesized samples are strongly depended on the hydrothermal temperature. The desired g-C_3N_4 nanosheets with a thickness of around 3 nm could be synthesized through an optimized 200 °C hydrothermal pretreatment. Compared to the bulk g-C_3N_4, the ultrathin g-C_3N_4 nanosheets possessed high specific surface area, large electronic band structure, and fast photoinduced electron-hole separation capability. As a consequence, the resultant nanosheets exhibited excellent visible-light-driven photocatalytic water splitting performance for hydrogen evolution (503 μmol h^{-1} g^{-1}), which is over 6 times higher than the bulk powder. This work highlights a feasible but simple strategy for the production of ultrathin graphite-like nanosheets and develops an efficient metal-free nanomaterial for application in energy conversion.

1. Introduction

Conversion and storage of solar energy into chemical fuels by photocatalytic hydrogen evolution has been considered as a green and sustainable technology for solving the increasingly serious energy concerns [1–3]. The clean and high energy capacity hydrogen fuel will play an essential role in development of a renewable future of human society in 21st century. Since the pioneering work by Honda and Fujishima in 1972 [4], numerous semiconductor photocatalysts have been reported for hydrogen evolution from water splitting [5], yet none of them are at a stage for industrial deployment [6]. What is more, most of these photocatalytic materials suffer from some obvious disadvantages, such as low photocatalytic activity under visible-light, lack of photochemical stability, complicated preparation processes, and associated with rare elements.

One promising material is graphitic carbon nitride (g-C_3N_4), an abundance metal-free photocatalyst, which has attracted extensive attention in the field of photocatalysis [6–12]. g-C_3N_4 can be easily prepared from the inexpensive precursors (melamine, dicyandiamide, urea or thiourea) and has a suitable bandgap potential for water redox under visible-light, good chemical stability, and tunable electronic properties [13–15]. Unfortunately, the photocatalytic efficiency of bulk g-C_3N_4 is seriously limited which are mainly attributed to the rapid electron-hole pair's recombination and low surface area causing by the π-π conjugated electronic system [16–19]. Although the photocatalytic activity of bulk g-C_3N_4 is far from satisfactory for photocatalytic applications, there are still significant approaches for performances improvement. The strategies to enhance photoreactivity include introducing heteroatoms [13,17,20–25] or functional groups [26–31], constructing heterojunctions with semiconductors [32–38] or metal nanoparticles [39–45], engineering nitrogen/carbon vacancies [18,46–49], driving protonation [24,50–52], and formation of nanoarchitectures [14,16,19,53–60]. Among them, nanostructures g-C_3N_4, especially, two-dimensional (2D) nanosheets with unique physicochemical properties have been widely emerged in photocatalytic reactions. Generally, the thermal oxidation etching [14,61,62] and ultrasonication-assisted liquid exfoliation [56,60,63]

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are two most popular approaches to prepare the g-C_3N_4 nanosheets from its bulk powders. Unfortunately, the thermal-oxidized reaction will generate abundant interface defects, and the liquid exfoliated nanosheets had rather low yield as well as possessed very time-consuming exfoliated processes [64].

It has been experimentally shown that one common and feasible methodology for obtaining of nanostructured g-C_3N_4 is to pretreat the nitrogen-rich precursors such as cheap melamine, then further thermal polymerization of the modified precursor [12]. For example, using hydrochloric acid, hydrogen peroxide, acetic acid, and phosphorous acid pretreatment of melamine for the synthesis of distinct nanoarchitectures g-C_3N_4 included platelet-like [65], porous network [66], laminated porous [67], and hexagonal tube [68] have been reported. More importantly, those g-C_3N_4 with different nanostructures can significantly ameliorate their physicochemical properties, leading to the promoting of photogenerated electron-hole pair's separation, enlargement of the surface area, and optimization of the photocatalytic activity. Besides, it is documented that the hydrothermal synthetic method is not only a bottom-up approach, but also plays a critical role in the controllable fabrication of various semiconductor nanomaterials [69]. However, to the best of our knowledge, the solely hydrothermal method for the pretreatment of melamine as precursor to prepare g-C_3N_4 nanosheets with high-efficiency photocatalytic activity has few been reported.

In this study, we firstly report an alternative but simple strategy to prepare the g-C_3N_4 nanosheets by directly thermal calcination of the hydrothermally pretreated melamine. Subsequently, the physicochemical properties of as-synthesized samples are strongly depended on the hydrothermal temperature, that is, higher temperature can obtain the desired g-C_3N_4 nanosheets with high-performance. The ultrathin g-C_3N_4 nanosheets with a thickness of approximately 3 nm could be successfully synthesized at an optimized 200 °C. In particular, the resultant nanosheets possessed a higher surface area, larger electronic band structure, and more effective charge carries transporting ability in comparison with the bulk g-C_3N_4. As a result, the ultrathin nanosheets exhibited dramatically improvement of photocatalytic performance for hydrogen evolution under visible-light irradiation ($\lambda > 420$ nm), which is over 6-folds higher than the bulk powder.

2. Experimental section

2.1. Synthesis of g-C_3N_4 nanosheets

The g-C_3N_4 nanosheets were prepared by thermal polymerization of the hydrothermal treatment melamine as precursors. Typically, 2.0 g melamine was dissolved in 30 mL water, and stirring for 30 min. Then, the suspensions were transferred to a 50 mL Teflon-lined autoclave and heated at 180, 190, 200, 210, and 220 °C for reaction 12 h, respectively. After being cooled to the room temperature, the white precursors were washed with distilled water and collected by drying in vacuum at 60 °C over night. Noting that there is no product when hydrothermal treatment of melamine at 210 °C or 220 °C, which suggested melamine can be hydrolyzed at higher hydrothermal temperature. Finally, the obtained precursors were put into a 50 mL alumina crucible with a cover, then heated in a muffle furnace in air atmosphere at a rate of 2.3 °C/min and kept for 4 h at 550 °C. After being cooled to room temperature, the resulting products were collected and labeled as g-C_3N_4(180), g-C_3N_4(190), and g-C_3N_4(200), respectively. For comparison, the formed melamine precursor at 200 °C also heated in N_2 atmosphere in tube furnace for preparation of the sample. Bulk g-C_3N_4 powders were also synthesized by directly thermal polymerization of 2.0 g melamine, which is similar to the above process expect the hydrothermal pretreating.

2.2. Characterization

The crystal structures were determined by powder X-ray diffraction (XRD, D/MAX-2500 diffractometer, Rigaku, Japan). The functional groups were determined by Fourier transform infrared (FT-IR, Nexus 470, Thermo Electron Corporation) using the KBr pellet technique at room temperature. The X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al Kα X-ray sources. The morphologies and microstructures were observed by using field emission scanning electronic microscopy (SEM, Hitachi, Japan), transmission electron microscopy (TEM, JEM-2100F, Japan), and atomic force microscopy (AFM, Asylum Research MFP930, America). The nitrogen (N_2) adsorption and desorption isotherms of the samples were measured by a NOVA 3000e (America) nitrogen adsorption apparatus. The UV–vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-2450 spectrophotometer using $BaSO_4$ as the reference. The photoluminescence (PL) spectra were analyzed with a Perkin-Elmer LS 55 at room temperature using a fluorescence spectrophotometer. The photocurrent measurements were investigated on a CHI-852C (CH Instrument) electrochemical workstation by a standard three-electrode system.

2.3. Photocatalytic hydrogen evolution test

The photocatalytic performance of as-prepared samples were evaluated by the water splitting for hydrogen evolution using the 300 W Xenon arc lamp with an optical filter ($\lambda > 420$ nm) as the visible-light source. Typically, 50 mg of photocatalysts were well dispersed in 200 mL of aqueous solution containing 10 vol% triethanolamine scavenger. Subsequently, a certain amount of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution was added for the *in-situ* formation of Pt as the co-catalyst, which yields a loading of around 3 wt%. Afterwards, the system was vacuumized to remove the dissolved oxygen in solution and the temperature was carefully maintained below 5 °C under the whole experiment. During the photocatalytic reaction, the evolved gas was collected at the given time intervals and analyzed by a Shimadzu GC-14C gas chromatography equipped with high-purity Ar carrier gas.

3. Results and discussion

The crystal structures of as-synthesized samples were characterized by XRD analysis. As shown in Fig. 1a, all of them depicted the two XRD diffraction peaks at around 13.0° (100) and 27.5° (002), which can be respectively corresponded to the in-plane structural packing motif and interlayer stacking of aromatic segments of graphite-like materials [7,9,10,16,35]. Through the hydrothermal process at different temperature, the (002) peaks of the as-prepared g-C_3N_4 samples are slowly up-shifted to 27.73° with respect to the bulk g-C_3N_4 (27.43°) (Fig. 1b), indicating the significant decreasing the gallery distance between the basic sheets from $d = 0.325$ nm for bulk g-C_3N_4 to $d = 0.322$ nm for g-C_3N_4(200) nanosheets [14]. Meanwhile, the (002) peaks of the as-obtained g-C_3N_4 samples become weaker and broaden with increasing the hydrothermal temperature. The similar phenomenon was also observed in the previously reported g-C_3N_4 nanosheets, demonstrating the nanosheets as we expected [56,60,63]. Moreover, the stronger and wider (100) peaks may be due to the g-C_3N_4 nanosheets prepared from the unique melamine precursors can effectively keep the hydrogen bonds in the intralayer framework [70], while the nanosheets exfoliated from bulk g-C_3N_4 usually can