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Porous graphitic carbon nitride nanosheets prepared under self-producing atmosphere for highly improved photocatalytic activity

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ABSTRACT

The reaction atmosphere employed in graphitic carbon nitride ($g—C_3N_4$) synthesis can play an important role in modifying the electronic structure and the properties of photoexcited charge carriers and consequently the photocatalytic activity of semiconductor photocatalysts. By controlling the entrance of N_2 in the preparation of $g—C_3N_4$, we introduced pyrolysis-generated self-producing atmosphere. Under the homogeneous self-producing atmosphere and without any other additives, we fabricated porous $g—C_3N_4$ with more uncondensed amino groups. These formed pores endow $g—C_3N_4$ nanosheets with more exposed active edges and cross-plane diffusion channels that greatly speed up mass and charge carrier transfer. Furthermore, the uncondensed amino groups within the structure could promote the dispersion behavior of samples in water and induce the structure distortion of $g—C_3N_4$ layers through the strong hydrogen bonding interactions between layers and thus decease the distance of interlayers. Enhanced photocatalytic activity is seen as well from a drastic increase in the degradation of rhodamine B (RhB) dye. This work provides a simple and efficient strategy for fabricating porous texture and realizing the tunable structure distortion of $g-C_3N_4$ layers to adjust its electronic structure and photocatalysis.

1. Introduction

Semiconductors based photocatalysis have gained considerable interdisciplinary interest for their great potential in environmental and energetic applications such as photocatalytic degradation of pollutants and photocatalytic hydrogen generation ever since the pioneering study coauthored by Fujishima and Honda in 1972 [1,2]. Among the numerous types of photocatalysts, graphitic carbon nitride ($g—C_3N_4$), since the first seminal report on $g—C_3N_4$ photocatalysts in the H_2 evolution was published in 2009 [3], has been considered as the next generation photocatalyst in the research communities, and also a step to achieving sustainability for artificial photosynthesis and environmental remediation [4]. As a metal-free polymeric photocatalyst, $g-C_3N_4$ which is constructed from N-bridged tri-s-triazine repeating units that form two-dimensional conjugated planes packed together via van der Waals interactions, exhibits many fascinating features, such as being metal-free, appealing electronic band structure and optical properties, high chemical and thermal stability, reasonable cost, "earth-abundant" nature, flexible supermolecular networks that allow for an ease in tuning material properties by alternating the chemical structure of backbones and so on [5,6]. However, bulk $g—C_3N_4$ materials prepared by direct polycondensation from nitrogen-rich precursors, are still suffer some obstacles to achieve high reactivity, especially the low specific surface area, the limited active sites, and low charge carriers separation and the serious aggregation during the photocatalytic process [7,8]. Thus, many strategies have been taken to enhance the photocatalytic activity of the bulk $g—C_3N_4$, for instance, morphology control [9], doping with heteroatoms [10,11], constructing heterostructures [12,13], fabricating copolymers [14,15] and so on. However, developing a simple approach to modify the intrinsic structures and improve photocatalytic properties of $g—C_3N_4$ is still desirable.

As for in-plane organization of tri-s-triazine units and the compression degree of aromatic planes, $g—C_3N_4$ is just a typical polymer that has adjustable chemical and textural structures for photocatalysis [3]. Texture, electronic, optical, and photocatalytic properties of $g—C_3N_4$ are strongly influenced by the condition of synthesis, such as the types of precursors [16], temperature-controlling route [17], pyrolysis temperature [18], duration employed in $g-C_3N_4$ synthesis [19] and so on. In addition, the characteristic properties and chemical structures of $g—C_3N_4$ are also strongly affected by the reaction atmosphere through inducing disordered structures, defects, and carbon and nitrogen vacancies [4]. Liu et al. intro-

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duced nitrogen by controlling the polycondensation temperature in static air [17]. Xiong et al. reported a high-yield synthesis of g—C_3N_4 products via heating of high vacuum-sealed melamine powder in an ampoule [20]. Tay and coworkers synthesized kinds of g—C_3N_4 in different atmosphere (air, N_2, forming gas (5%H_2 + 95% Ar) and pure H_2), and presented defect engineered g—C_3N_4 nanosheets produced by hydrogen treatment [21]. The hydrogenated defects in g—C_3N_4 were also prepared by high temperature H_2 treatment of bulk carbon nitride [22]. An amorphous g—C_3N_4 with a band gap of 1.90 eV was obtained by simply heating partially crystalline g-C_3N_4 in an argon atmosphere [23]. In addition, Liang et al. synthesized holey g—C_3N_4 nanosheets with abundant in-plane holes by thermally treating bulk g-C_3N_4 under an NH_3 atmosphere [7].Very recently, Li and coworkers prepared macroscopic foam-like holey ultrathin g-C_3N_4 nanosheets by self-modification of polymeric melon units under an air atmosphere, and drastically improved visible-light photocatalysis [24]. These fruitful findings encourage us to think about to develop a facile method in preparing a new and high efficient photocatalytical g—C_3N_4 material through self-modification under proper atmosphere.

As exposed, synthesizing of g—C_3N_4 undergoes a condensation process with ammonia losses under thermal treatment of nitrogen-rich precursors such as urea, thiourea, melamine, cyanamide, dicyandiamide, and so forth [4,25]. And several researchers found g—C_3N_4 samples by NH_3-mediated polymerization process or NH_3-treated had a high porosity and specific surface area, showing better photoactivity than the corresponding bulk g—C_3N_4 [7,26,27]. So we expect designing a simple and facile way to take advantage of retainable self-producing atmosphere-NH_3 during pyrolysis to fabricate self-modified g—C_3N_4. Here, we report a facile, convenient, and most importantly simple approach to create NH_3 atmosphere by controlling the entrance of N_2 atmosphere to synthesize porous graphitic carbon nitride nanosheets with more uncondensed amino groups, as shown in Fig. 1. These formed holes endow g—C_3N_4 nanosheets cross-plane diffusion channels that greatly speed up mass and photogenerated charge transfer. Meanwhile, these holes also provide numerous boundaries in favor of decreasing the aggregation, and more exposed active edges to promote photocatalysis. In addition, the uncondensed amino groups within the structure could generate the strong hydrogen bonding interactions between layers and thus induced the structure distortion of g—C_3N_4 layers. As expected, compared with the bulk g-C_3N_4, the obtained self-modified g—C_3N_4 show remarkably enhanced photocatalysis in the degradation process of RhB under light irradiation.

2. Experimental section

2.1. Sample preparation

The bulk g—C_3N_4 sample was prepared by a previously reported thermal polymerization method [28]. In a typical procedure, the material was synthesized typically by heating 2.5 g of melamine in a semi-closed alumina crucible with a cover under N_2 gas flow to 550 °C for 4 h at a heating rate of 5 °C/min, followed by naturally cooling to room temperature. The product was collected and ground into powder and denoted as CN—N.

The self-modified g—C_3N_4 materials were prepared mostly the same as CN—N, except stopping the entrance of N_2 at temperature of 500, 300, and 100 °C. The obtained samples were denoted as CN-5, CN-3, and CN-1.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was collected by a Rigaku Dmax/Ultima IV diffractometer with monochrommatized Cu ka radiation (k = 1.5418 Å). Fourier transform infrared (FT-IR) spectroscopy was performed on a Perkin-Elmar model 2000 FTIR spectrophotometer. Scanning electron microscopy (SEM) was taken with a JEOL JSM-6510LV scanning electron microscopy. X-Ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 Xi with a high-performance Al monochromatic source ($h\upsilon$ = 1486.6 eV, 150 W). All binding energies were referenced to the C 1s peak at 284.8 eV of surface adventitious carbon, and the elemental compositions were determined from peak area ratios after correction for the sensitivity factor for each element. And UV–vis diffuse reflectance spectra (DRS) was recorded on a Shimazu UV-3600 spectrophotometer equipped with diffuse reflectance accessories, using $BaSO_4$ as the reference sample. Brunauer-Emmett-Teller (BET) surface area was calculated from N_2 adsorption-desorption isotherms collected at 77 K using Quantachrome Instruments version 3.0. The photoluminescence (PL) spectra of photocatalysts were detected on a Varian Cary Eclipse spectrometer with excitation wavelength of 350 nm.

2.3. Photocatalytic tests

The photocatalytic activities of the prepared samples were measured by degrading RhB at ambient temperature in air with magnetic stirring. The UV–visible light was provided by a 70 W metal halide that was often used in photocatalysis conveniently [29–32]. For the degradation of RhB, 40 mg of photocatalyst was added to 80 mL of RhB aqueous solution (10 mg/L) at room temperature. Prior to irradiation, the mixture of photocatalyst and RhB suspension was firstly sonicated for 10 min and then magnetically stirred for 20 min in the dark to obtain an adsorption-desorption equilibrium. At certain time intervals, about 3 mL sample was taken out from the reaction system and centrifuged to remove the photocatalyst powders for analysis. The absorbance of the supernatant was measured using a Shimadzu UV-2550 UV–vis spectrophotometer. The relative concentration (C/C_0) of the RhB solution was calculated at 554 nm C_0 and C are the concentrations of RhB at the beginning of light irradiation and at time t, respectively.

The cyclic runs of RhB degradation was carried out to verify the stability of CN-3. After each cycle, the catalyst was collected by centrifugation, washed with distilled water, dried and then used in the next cycle without weighing. Then the photocatalytic activity was again tested.

2.4. Active species detection

The reactive oxidative species in the photodegradation were detected using in situ trapping experiments. The detection process was similar to the photodegradation experimental process. Three different scavengers, such as *p*-benzoquinone (BQ, $^{\bullet}O_2^-$ radicals scavenger, 1.0 mM), ammonium oxalate (AO, holes scavenger, 1.0 mM) and isopropanol (IPA, $^{\bullet}OH$ radicals scavenger, 1.0 mM), were added to the RhB solution prior to illumination in three separate photodegradation systems [31,32].

3. Results and discussions

3.1. Structural characteristics

The XRD patterns of the bulk and modified g—C_3N_4 are displayed in Fig. 2. Typically, two individual well-resolved peaks can be determined for CN—N. The strong peak at 27.2° corresponding to an inter-planar distance of approximately 0.324 nm was characterized for (002) reflection of graphitic layered materials, whereas the weak one at 13.0° (d = 0.685 nm) for (100) reflection can be attributed to the in-plane structural packing motif of tri-s-triazine units. After stopping the entrance of N_2, the graphitic-like structure of g—C_3N_4 was retained without an impurity phase [3]. However, the main