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Synthesis and photocatalytic performance of g-C_3N_4 nanosheets via liquid phase stripping

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ABSTRACT

Well dispersed g-C_3N_4 nanosheets were prepared by exfoliating the bulk g-C_3N_4 in concentrated sulfuric acid. Phase structures, morphologies and elemental compositions were characterized by X-ray diffractometer, scanning electron microscope, transmission electron microscope and X-ray photoelectron spectrometer, respectively. Optical absorption and photoluminescence were also used to explain the optical performances of samples. NaI, BQ and IPA were used as the sacrificial agents for studying the surface reactions in the photocatalytic process. By the precipitation of g-C_3N_4 nanosheets in ethanol with different ratios between concentrated sulfuric acid and ethyl alcohol, well dispersed g-C_3N_4 nanosheets with high specific surface area can be obtained. The optimized g-C_3N_4 (1:10) nanosheets achieve the highest photocatalytic activities under UV light illumination, which can degrade 10 mg/L RhB about 98% in 60 min, which is 6 times that of bulk g-C_3N_4 under UV light.

1. Introduction

The g-C_3N_4 has attracted considerable attention of many scholars due to its unique properties derived from electronics, sensors, catalysts and energy storage [1,2]. Since the potential energy of N 2p orbits is higher than that of O 2p orbits [3], and nitrides have a smaller bandgap, increasing studies were focused on the visible light response of g-C_3N_4 [4,5]. The bulk g-C_3N_4 can be prepared by calcinating urea, dicyandiamide, melamine [6] and other s-triazine heterocyclic compounds [7] by the sublimation and transformation method. The bandgap of the bulk g-C_3N_4 is 2.7 eV and can consequently absorb light with wavelength to 450 nm [8]. However the photocatalytic performance of bulk g-C_3N_4 is unsatisfactory due to its high recombination rate of photon-generated electron-hole pairs, low absorption as well as small surface area. In recent years, many synthetic techniques and effective modification procedures have been proposed to optimize the photoactivity of g-C_3N_4 [9], such as electronic structure modulation [10], nanostructure design [11], crystal structure engineering [12], and heterostructure construction [13].

It is reported that bulk g-C_3N_4 possesses the layered structure which are similar to graphite, where the C–C bonds were replaced by strong covalent C–N bonds in every layer and the layers were connected by weak van der Waals force [14]. Due to the above characteristics of bulk g-C_3N_4, it seems that the bulk g-C_3N_4 is easy to be exfoliated into a monolayer or a few layers of g-C_3N_4 [15]. So it is possible to obtain so-called g-C_3N_4 nanosheets from bulk g-C_3N_4. Wang et al. firstly reported the reversible protonation of carbon nitride by stirring with strong mineral acids (37% HCl) for 3 h [16]. Qiao et al. reported proto-functionalized g-C_3N_4 nanosheets with a large specific surface area of 305 $m^2\ g^{-1}$[17]. Xie et al. exfoliated the bulk g-C_3N_4, and obtained the graphitic-phase C_3N_4 nanosheets for bioimaging [18]. Through the thermal oxidation “etching” method, Cheng et al. get the g-C_3N_4 nanosheets to improve photocatalytic activities [19]. However, there is no agreed conclusion on the structure of g-C_3N_4, whether the g-C_3N_4 nanosheets have been shaped, during the exfoliation process. And, effective routes should be developed for preparing the nanosheets of g-C_3N_4.

As we all know, owing to strong dehydrating and oxidizing properties, concentrated sulfuric acid is highly corrosive liquid on many substances. The mechanism of the thermal oxidation etching is that the hydrogen-bonds connecting the polymeric melon units in the layers are not stable enough against protonation. And the van der Waals force between the layers will also be broken due to the intercalation reaction of SO_4^{2-}. The bulk g-C_3N_4 will be gradually oxidized, resulting in the different thickness of g-C_3N_4, which will reach the desired nanoscale. Here, we get well dispersed g-C_3N_4 nanosheets by direct protonizing the bulk g-C_3N_4 using concentrated sulfuric acid (be also called liquid phase stripping) in air, which possesses the advantages of low cost,

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easy getting, security and environmental friendly. The obtained nanosheets were investigated in terms of feature, crystal structure, electronic structure and photocatalytic activity. The g-C_3N_4 nanosheets with flake structures possess much better photocatalytic performances in UV light than that of bulk g-C_3N_4.

2. Experimental

2.1. Chemicals

Melamine ($C_3N_6N_6$), concentrated sulfuric acid (98%), ethyl alcohol (C_2H_6O) and rhodamine B (RhB) were purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used as received without further purification.

2.2. Synthesis

g-C_3N_4 was synthesized by solid sublimation and transformation. In a typical procedure, 4–10 g melamine was putted into a corundum boat and the other boat was used as a lid. Then, the two boats were wrapped by aluminium-foil paper, for avoiding volatilizing in the process of calcining in the muffle furnace (OTF-1200X). The melamine in corundum boat were calcined at 550 ℃ for 4 h with the heating rate of 8 ℃/min and the initial temperature was 22 ℃. Finally, the luminous yellow bulk g-C_3N_4 was obtained by grinding the calcinate at room temperature.

The well dispersed g-C_3N_4 were obtained by dissolution and reprecipitation in H_2SO_4 solution, and the synthesis process was shown in Fig. 1. 50 mg bulk g-C_3N_4 powders were dispersed in 1 ml concentrated sulfuric acid solution at 90 ℃ for 5 h with stirring for complete disolution. The luminous yellow solution can be obtained after the complete dissolution of bulk g-C_3N_4 powders in H_2SO_4 solution.

The g-C_3N_4/H_2SO_4 solution was added into ethanol with different volume ratios of 1:1, 1:5 and 1:10, respectively. White product will precipitate from the mixed solution slowly with continuous stirring. Then, the products were separated with centrifugation and washed with ethanol several times to remove the chemical remnants. Subsequently, the obtained products were put into drying over at 40℃for 12 h. And the products prepared with different volume ratios of H_2SO_4/ethanol were defined as g-C_3N_4 (1:1), g-C_3N_4 (1:5) and g-C_3N_4 (1:10), respectively.

2.3. Characterizations and instruments

The phase structures of the samples were measured by using an X-ray diffractometer (D/MAX2500 V) using Cu Kα radiation with 2θ ranging from 10° to 90°. Morphologies of the samples were observed with a SU8020 field emission scanning electron microscope and a JEM-2100F high resolution transmission electron microscope. The samples were prepared by dispersing the powder in ethyl alcohol, and carbon-coated copper grids were used as sample holders. X-ray photoelectron spectroscopy analysis of the samples was performed using an ESCALAB 250 photoelectron spectrometer with a monochromatic Al Kα X-ray beam (1486.60 eV). The optical absorption performance of the samples was evaluated by using a diffuse reflectance spectrometer (UV3600, Shimadzu) using $BaSO_4$ as the reference.

The photocatalytic tests were conducted using an XPA-7 photochemical reactor (Nanjing Xujiang Machine-electronic Company, China) with a 300 W high-pressure mercury lamp as the UV light source (maximum emission wavelength at 365 nm in the UV region). An optical filter with a cut off wavelength at 400 nm was used to eliminate the visible light. Similarly, a 250 W high-pressure halogen lamp was the visible light source with optical filters to prevent ultraviolet light under 420 nm. In addition, the analytical apparatus was UV-1800 ultraviolet and visible spectrophotometer (Shimadzu, Japan).

The rinsing steps were performed by using a TGL-16 G centrifugal machine (Shanghai Anting Scientific Instrument Factory, China) combined with 7 ml centrifugal tubes.

2.4. Photocatalytic property

The photocatalytic properties by degrading RhB solution were evaluated. The resuspensions were placed in the dark environment for 30 min to achieve the equilibrium of absorption/desorption. The photocatalytic degradation of RhB solution was performed in the XPA-7 photochemical reactor with the distance between the suspension and the light source of 10 cm. After being illuminated successively for 30, 60, 90 and 120 min, respectively, a 5 ml solution was collected from the suspension and was centrifuged. Then, the upper solution was measured by using a UV1800 spectrometer for measuring the concentration of RhB. There was a standard linear relation between absorbancy A and concentration C of RhB in the solution based on the Lambert–Beer law: $D=(C_0-C)/C_0=(A_0-A)/A_0\times100\%$ (A_O – original absorbancy, A – absorbancy after irradiation), in which C is the remnant RhB concentration after being degraded in a given time, and C_O is the initial

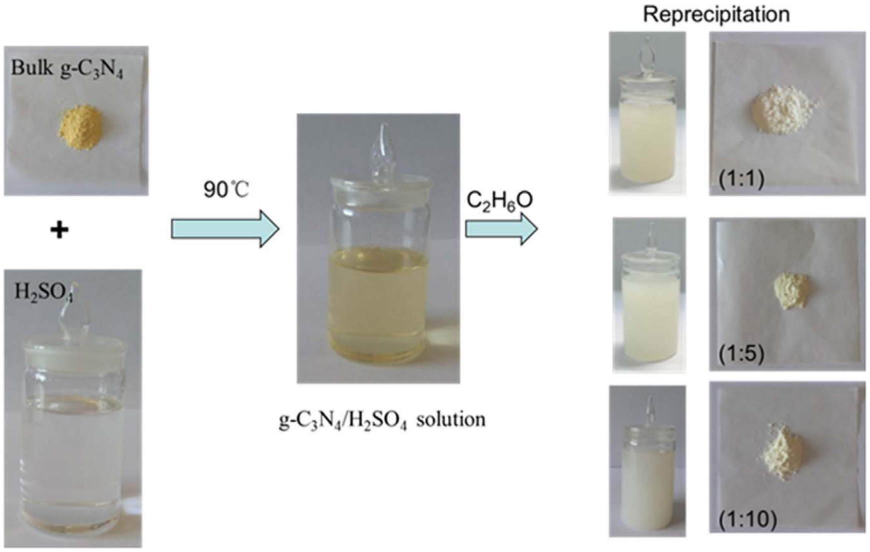

Fig. 1. Synthesis procedure of well dispersed g-C_3N_4 nanosheets.