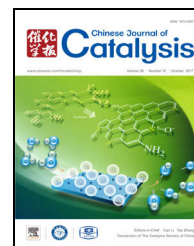


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Article

One-step synthesis of graphitic carbon nitride nanosheets for efficient catalysis of phenol removal under visible light



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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) nanosheet photocatalysts were synthesized via a facile impregnation-thermal method. The as-prepared materials were characterized and investigated as metal-free photocatalysts for the degradation of phenol in aqueous solution under visible light. Results revealed that the g-C₃N₄ nanosheets exhibited a 78.9% degradation for phenol after 30 min, which was much faster than that of the pristine g-C₃N₄. Using Brunauer-Emmett-Teller theory, the surface area of g-C₃N₄ nanosheets was 103.24 m²/g, which was much larger than that of g-C₃N₄. The larger surface area increases the contact area of the material with phenol, enhancing the photocatalytic activity. These results highlight the potential application of sustainable metal-free photocatalysts in water purification.

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1. Introduction

The field of heterogeneous photocatalysis has developed rapidly in the last four decades as governments and scientists research green and sustainable technologies [1,2]. Semiconductor-based photocatalysis requires only light as a driving force. A suitable semiconductor as a photocatalyst has been used in catalytic reactions for a variety of applications, such as hydrogen production from water splitting [3], CO₂ reduction into hydrocarbonfuels [4], decomposition and mineralization of organic pollutants [5], selective organic synthesis [6], and disinfection of bacteria [7]. Semiconductor-based photocatalysis has emerged with valuable metal-based semiconductors; however, they are active only in the ultraviolet region and have moderate performances.

Graphitic carbon nitride (g-C₃N₄) is the most stable allotrope among various carbon nitrides (CNs) under ambient conditions. Unlike TiO₂, which is only active in the UV region, g-C₃N₄ possesses a bandgap of ca. 2.7 eV [8,9], which enables it

to be a visible-light active photocatalyst for a range of reactions. More importantly, g-C₃N₄ is only composed of two earth-abundant elements: carbon and nitrogen, suggesting that it can be easily prepared at low cost [10,11]. Moreover, its polymeric nature allows control over the surface chemistry via molecular-level modification and surface engineering. The unique aforementioned characteristics of g-C₃N₄ make this material a very promising photocatalyst for various applications [12]. Great and fruitful efforts have been made on g-C₃N₄-based photocatalysis [13]. However, pristine g-C₃N₄ still suffers from unsatisfactory photocatalytic efficiency because of its restricted visible-light harvesting capacity, ready recombination of charge carriers, and low surface area [13–21].

Many researchers have put great effort of preparing g-C₃N₄ nanostructures (synthetic routes [22–24], thermal exfoliation [25–27], and templates [28]). For example, Shalom et al. [23] reported a new and simple synthetic pathway to form ordered, hollow CN structures, using a cyanuric acid-melamine complex in ethanol as a starting product. Yang et al. [24] demonstrated a

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biotic precursor approach of g-C₃N₄ polymers synthesized from urea and nucleobases. Yang et al. [27] reported a facile and green approach to prepare few-layered polymeric CN semiconductors by a one-step carbon/nitrogen steam reforming reaction. g-C₃N₄ can be imprinted with a twisted hexagonal rod-like morphology by a nanocasting technique using chiral silicon dioxides as templates [28]. Ou et al. [29] fabricated crystalline CN nanosheets by exfoliation of bulk tri-s-triazine-based crystalline CN powder in isopropanol via sonication for 15 h. Guo et al. [30] presented a facile synthesis method (the mixture of glucose, boric acid and urea) to produce a porous structure of two-dimensional boron CN nanosheets. In the results of the above-mentioned studies, g-C₃N₄ exhibited dramatically enhanced visible-light photocatalytic activity toward hydrogen evolution and pollutant degradation. A potential scale method for preparing g-C₃N₄ nanosheets remains a challenge.

In this work, we developed a simple method to prepare g-C₃N₄ nanosheets by thermal polymerization of cyanuric acid and melamine in air. These g-C₃N₄ nanosheets may show superior photocatalytic activities compared with the bulk g-C₃N₄. The photocatalytic activity of g-C₃N₄ is evaluated toward phenol degradation under visible-light irradiation and compared with that of g-C₃N₄.

2. Experimental

2.1. Chemicals and materials

Melamine, cyanuric acid, phenol, and methanol were purchased from Sinopharm (Shanghai, China). All chemicals were of analytical grade and used without further purification. All aqueous solutions were freshly prepared with deionized water.

2.2. Synthesis of g-C₃N₄(x)

All g-C₃N₄ samples were synthesized using melamine and cyanuric acid as the starting material through a stage programming heating approach. The starting material was heated to 550 °C at a heating rate of 2 °C/min and held at this temperature for 4 h. The sample was denoted as g-C₃N₄(x), where x refers to the molar ratio of melamine and cyanuric acid.

For comparison, bulk g-C₃N₄ was prepared through a widely-used one-step polycondensation process. Briefly, 2 g of MA was directly heated to 550 °C in air and kept for 2 h.

2.3. Characterization

Scanning electron microscopy was performed with a FEI Nove NanoSEM 230 field emission system on loose and lightly pressed samples. X-ray diffraction patterns were measured on a Rigaku 2500 diffractometer with Cu-K α radiation ($\lambda = 0.15406$ nm) at a scan rate of 8°/min. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a ThermoFisher-VG Scientific instrument with an Al-K α (1486.6 eV) monochromatic X-ray radiation (operated at 200 W) from a twin anode in the constant analyzer energy mode with an energy of 30 eV. The UV-vis absorption spectra were measured on a Shimadzu

UV2550 spectrophotometer using BaSO₄ as the reflectance standard.

2.4. Photocatalytic performance evaluation

Photodegradation of a phenol solution (50 mg/L) was performed to evaluate the photocatalytic performance of the synthesized catalysts in a top-window Pyrex cell with the temperature maintained at 20 °C by a circulating water system. The catalyst (50 mg) was added into the phenol solution (100 mL). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure phenol adsorption/desorption equilibrium. The suspension was irradiated by a 300 W Xe lamp with a cut off filter (<400 nm) and an irradiation intensity of 100 mW/cm². At given time intervals, aliquots of the irradiated suspension were collected, centrifuged, and analyzed on a Shimadzu LC-20AT high-performance liquid chromatography system with an SPD-20A column. The detection wavelength was 280 nm. The mobile phase was a mixture of methanol and water with a volume ratio of 70:30 and a flow rate of 1 mL/min.

3. Results and discussion

The one-step pyrolysis of the precursor melamine showed decreased yields of the products as the molar ratio of melamine to cyanuric acid was varied from 1:0 to 1:9. Cyanuric acid is totally decomposed in these conditions. The appearance of the sample looked like messaline with characteristics associated with the delamination and crystal-structural alternation within the CN polymers [26,31].

Fig. 1 shows the scanning electron microscopy images of all samples. Many flakes with laminar morphologies were observed. However, the bulk g-C₃N₄ showed no exfoliation with irregular particles. The product after thermal exfoliation presented in Fig. 1 displayed a layer structure with some fabric-like surface. Fig. 2 shows a representative atomic force microscopy image of the g-C₃N₄(1:9) nanosheets. The lateral size of these sheets ranged from tens of nanometers to several micrometers. The thickness analysis of the nanosheets revealed a thickness of about 3.0 nm.

As cyanuric acid decomposed, the appearance of CN became mainly atomic layers with a thin, glossy, and transparent texture (Fig. 1). Moreover, from the detailed view of the sample, a distinct curved nanodomain was displayed at the edge of the large plane (Fig. 1). Such a structural distortion of 2D crystals has been demonstrated to stabilize the 2D structure, as also observed in single-layered graphene, which may be stabilized by the formation of finite-sized ripples [32,33].

Fig. 3 shows X-ray diffraction patterns of all the samples with a characteristic peak at 27.48° ($d = 0.326$ nm), corresponding to the (002) interlayer reflection of g-C₃N₄. The peak at 27.48° was weaker than those of the sample obtained by bulk polymerization at 550 °C, which indicated that the interlayer structure was destroyed after thermolysis. Moreover, the peak at 27.48° (attributed to the in-plane repeated tri-s-triazine units) become narrow with increased reaction temperature. The evolution of the curved shape and curls during the assem-

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