



Graphitic carbon nitride nanosheets as highly efficient photocatalysts for phenol degradation under high-power visible LED irradiation

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ABSTRACT

Exfoliated g-C₃N₄ materials were prepared by thermal treatment of bulk materials synthesized from melamine at 4 different temperatures in range from 500 to 600 °C. The exfoliated g-C₃N₄ synergically increased the photocatalytic degradation of phenol as effects like the fast production of H₂O₂, the presence of more active holes for direct phenol degradation and the use of high-power visible (416 nm) LEDs as irradiation source. The amount of phenol initially present was 99% converted in 15 min. All materials were also tested for comparison only in UVA region by using high-power UV (370 nm) LEDs. All prepared materials were thoroughly characterized by several analytical methods.

In this work, the combination of g-C₃N₄ after thermal treatment and high-power visible LEDs reduced the time needed for complete phenol degradation from several hours to just a few minutes. The mechanism of phenol degradation was also studied by introducing different active species scavengers into the reaction medium.

1. Introduction

Graphitic carbon nitride, a promising conjugated polymer semiconductor, has been used in many photocatalytic applications including hydrogen production by water splitting [1–3], CO₂ and NO_x reduction [4–6], organic pollutants degradation [7–9] or organic synthesis [10]. Low-cost and metal-free sunlight-driven g-C₃N₄ is chemically and thermally stable and it does not subject to photocorrosion during photocatalytic reactions contrary to another visible-driven semiconductor photocatalysts, e.g. CdS [11], CuO [12] or Ag₃PO₄ [13]. Enhanced photocatalytic activity was achieved by co-doping of g-C₃N₄ with cobalt [14], oxygen [15], gold [16] phosphorus [17] and also by coupling g-C₃N₄ with other semiconductor nanomaterials such as Bi₂O₄ [18], Cu₂O [19], SnO₂ [20], WO₃ [21] and TiO₂ [6,22]. Its photocatalytic activity is also improved by exfoliation of basic bulk material. Several methods for exfoliation such as liquid exfoliation [23], thermal exfoliation [24] or chemical exfoliation [25,26] were already successfully performed. Compared with bulk g-C₃N₄, the resulting nanosheet-

like materials exhibited enhanced photoabsorption and significantly larger surface area and different oxygen reduction pathway during photocatalytic reactions [27].

Lima et al. [10] studied morphological and chemical properties of bulk g-C₃N₄ modified by different exfoliation methods (chemical, mechanical and thermal treatment). Both mechanical and chemical treatments introduced structural and chemical defects (oxygen functionalities) in g-C₃N₄. Further, the specific surface area of exfoliated g-C₃N₄ was the highest after thermal treatment. This result was also confirmed by our previous research [28] in which we studied thermal treatment of bulk g-C₃N₄ at 500 °C and also g-C₃N₄, which was subjected to ultrasonication in water. The heating was found to be the more effective exfoliation procedure than ultrasonication.

Hydrogen peroxide can be considered a green oxidant for water purification and is widely used in photo-Fenton reactions (Fe²⁺, Fe³⁺/H₂O₂) for generating hydroxyl radicals (HO·). The disadvantage of this reaction is based on the required pH that must be very acidic, typically pH < 3 [29]. Zhang et al. [30] recently confirmed the production of

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H₂O₂ on surface of exfoliated g-C₃N₄ during phenol degradation by formation of 1,4-endoperoxide species by hypothesis of two-electron reduction of O₂.

Typical light sources used in photocatalytic oxidation reactions using g-C₃N₄ are mostly xenon lamps with cut-off filters at 400 nm [31] or 420 nm [32,33] for simulating solar light or mercury UV lamps with emission maximum wavelength at 365 nm [34]. All these light sources have several drawbacks such as high price, low intensity, overheating, short life span, etc. A good alternative to these light sources are light emitting diodes, which are relatively cheap, have narrow emission band (normally around 20 nm of full width at half maximum, FWHM) and are more energy efficient for photocatalytic reactions.

Phenol was chosen as a model compound to test the synthesized materials because its photodecomposition mechanism is well documented in the literature [35,36], there are reliable analytical methods for its determination, and because phenol is a widely spread organic pollutant and new finding can help to understand its behaviour in the environment.

The novelty of the present work lies in the development of a highly-efficient photocatalytic process based on metal-free g-C₃N₄ nanosheet catalysts with enhanced activity towards phenol degradation and simultaneous production of H₂O₂, using a low-cost and energy-efficient irradiation source (visible high-power LEDs).

2. Experimental

2.1. Preparation of materials

2.1.1. Reagents and materials

Melamine ($\geq 99\%$), 1,4-benzoquinone (1,4-BQ, 99.5%) and catechol (98%, HPLC grade) were purchased from Fluka; high-purity analytical grade *tert*-butanol (t-BuOH, $\geq 99.7\%$), hydroquinone (99%) and titanium(IV) oxysulfate (~ 15 wt.% in dilute sulfuric acid) were obtained from Sigma-Aldrich; triethanolamine (TEOA, 99%) was purchased from Panreac. All the reagents were used without further purification. Aeroxide TiO₂ (TiO₂ P25, Evonik) was used as received. Methanol (HPLC grade, VWR Chemicals) and ultra-pure water (Direct-Q Millipore system) were used for high performance liquid chromatography (HPLC).

2.1.2. Synthesis of bulk g-C₃N₄

All bulk g-C₃N₄ materials were prepared by direct heating of melamine. In every preparation method 5 g of melamine was placed into an alumina crucible with cover and heated in a muffle furnace. The heating rate was set at 3 °C min⁻¹ and the material was kept at the desired temperature 500, 525, 550 and 600 °C for 4 h. Materials were denoted as B500, B525, B550 and B600, respectively. In our previous research [37] melamine was heated at final temperature for 2 h. Due to narrower temperature ranges between materials, in this work, the precursor was left at the final temperature for 2 more hours (total of 4 h) for guaranteeing the materials properties, which could be affected by the little difference between the used temperatures. After cooling naturally to room temperature, the resulting yellow powder was ground in a mortar into a fine powder.

2.1.3. Synthesis of g-C₃N₄ nanosheets

The g-C₃N₄ nanosheets (NS) were prepared via thermal exfoliation of bulk materials at 500 °C for 2 h in air with a heating rate of 2 °C min⁻¹. The resulting materials were denoted as NS500, NS525, NS550 and NS600, depending on the temperature used in the thermal polymerization of starting bulk material. All the obtained materials show a pale colour comparing to the starting bulk materials.

2.2. Materials characterization

XRD patterns were recorded using a Bruker D8 Advance

diffractometer (Bruker AXS) equipped with a source of the CuK α radiation ($\lambda = 0.15406$ nm) and fast position sensitive detector LynxEye. The measurements were performed in the reflection $2\theta/\theta$ geometry, step mode with step 0.015° 2 θ and 43 s per step. Powder materials were pressed in a rotational holder and their phase composition was evaluated using PDF 2 Release 2011 database (International Centre for Diffraction Data).

Analysis of particle size distribution was performed by the DLS method using a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd, UK).

The specific surface area of the powder materials was determined by analysis of N₂ adsorption isotherms at 77 K using the BET method, in a Quantachrome NOVA 4200e multi-station apparatus.

Scanning electron microscopy was performed using a micro-scope Quanta FEWG 450 equipped with detectors EDS Apollo X (EDAX), ETD and BSE and with a camera EBSD HIKARI (EDAX). Before the SEM analysis the samples were sputtered with gold (Polaron Range SC 7640) in the argon atmosphere.

High resolution transmission electron microscopy was performed on a JEM 220FS microscope (Jeol, Japan) with an LaB₆ electron gun operating at 200 kV. The samples were dispersed in ethanol and then sonicated for 5 min. One drop of this dispersion was placed on a copper grid with a holey carbon film and dried at room temperature.

IR spectra of materials were measured by the potassium bromide pellets technique. Exactly 1.0 mg of material was ground with 200 mg dried potassium bromide. This mixture was used to prepare the potassium bromide pellets. The pellets were pressed by 8 tons for 30 s under vacuum. The IR spectra were collected using FTIR spectrometer Nexus 470 (ThermoScientific, USA) equipped with DTGS detector. The measurement parameters were the following: spectral region 4000–400 cm⁻¹, spectral resolution 4 cm⁻¹; 64 scans; Happ-Genzel apodization. Treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure potassium bromide.

The optical absorption of the powder solids was obtained by measuring the respective UV–vis spectra in a Jasco V-560 UV–vis spectrophotometer, equipped with an integrating sphere attachment (JASCO ISV-469). The spectra were recorded in diffuse reflectance mode and transformed by the instrument software (JASCO) to equivalent Kubelka-Munk units.

Photoluminescence spectra were measured by a spectrometer FLS920 (Edinburgh Instrument Ltd, UK). The spectrometer was equipped with a 450 W Xenon lamp (Xe900). The excitation wavelength was 370 nm. The width of excitation and emission slits was 0.4 nm and emission spectra were measured in the range from 390 to 700 nm.

2.3. Photocatalytic activity test

The phenol decomposition was carried out in a glass reactor (glass transmittance of 74%, see Supplementary Information, Fig. SI1) with a maximum capacity of 100 mL. The reactions were performed under UV or visible light using 10 W LEDs with an emission line peaking at 370 (FWHM = 10 nm) or 416 nm (FWHM = 17 nm, see Supplementary Information, Fig. SI2), respectively located symmetrically from the outside at 4.0 cm from the reactor wall. The average nominal irradiance of each UV or visible LED reaching the reactor was 37.9 or 112.6 mW cm⁻², respectively.

In a typical experiment, the catalyst load was kept at 1 g L⁻¹ and the initial phenol concentration at 20 mg L⁻¹. Before the irradiation, 50 mL of aqueous suspension containing phenol and the catalyst were put into an ultrasound bath and sonicated for 10 s and then stirred in the dark for 15 min in the case of bulk materials and for 1 h in the case of exfoliated materials before the LEDs were switched on to provide good homogenization of the dispersion and to reach the adsorption-desorption equilibrium in the whole system. During the photocatalytic reaction, air was continuously bubbled through the suspension.

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