



Graphitic carbon nitride: Synthesis, characterization and photocatalytic decomposition of nitrous oxide



Petr Praus^{a, b, *}, Ladislav Svoboda^{a, b}, Michal Ritz^b, Ivana Troppová^a, Marcel Šihor^a, Kamila Kočí^a

^a Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17. Listopadu 15/2172, Ostrava 708 33, Czech Republic

^b Department of Chemistry, Faculty of Metallurgy and Materials Engineering, VŠB-Technical University of Ostrava, 17. Listopadu 15/2172, Ostrava 708 33, Czech Republic

HIGHLIGHTS

- Graphitic carbon nitride (g-C₃N₄) was thermally synthesized from melamine in the range of 400–700 °C.
- The optimal temperature was determined at 600–650 °C.
- All synthesis products were properly characterized by physico-chemical methods.
- Exfoliation of g-C₃N₄ at above 600 °C was observed.
- g-C₃N₄ was used for the photocatalytic decomposition of N₂O.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 August 2016

Received in revised form

8 January 2017

Accepted 6 March 2017

Available online 8 March 2017

Keywords:

Graphitic carbon nitride

Melamine

Exfoliation

Photocatalysis

Nitrous oxide

ABSTRACT

Graphitic carbon nitride (g-C₃N₄) was synthesized by condensation of melamine at the temperatures of 400–700 °C in air for 2 h and resulting products were characterized and finally tested for the photocatalytic decomposition of nitrous oxide.

The characterization methods were elemental analysis, UV–Vis diffuse reflectance spectroscopy (DRS), photoluminescence (PL), Fourier transform infrared (FTIR) and Raman spectroscopy, measurement of specific surface area (SSA), X-ray powder diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy. The XRD patterns, FTIR and Raman spectra proved the presence of g-C₃N₄ at above 550 °C but the optimal synthesis temperature of 600–650 °C was found. Under these conditions graphitic carbon nitride of the overall empirical composition of C₆N₉H₂ was formed. At lower temperatures g-C₃N₄ with a higher content of hydrogen was formed but at higher temperatures g-C₃N₄ was decomposed. At the temperatures above 650 °C, its exfoliation was observed.

The photocatalytic experiments showed that the activity of all the samples synthesized at 400–700 °C was very similar, that is, within the range of experimental error (5 %). The total conversion of N₂O reached about 43 % after 14 h.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Graphitic carbon nitride has been considered a very promising semiconductor material [1], having been intensively studied during the last decade [2,3]. This material has diamond-like mechanical

* Corresponding author. Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17. Listopadu 15/2172, Ostrava 708 33, Czech Republic.

E-mail address: petr.praus@vsb.cz (P. Praus).

properties and is thermally, chemically and photochemically stable due to its tri-*s*-triazine (C₆N₇)-based building blocks and strong covalent bonds between carbon and nitrogen atoms. The important property of g-C₃N₄ is its band gap of about 2.7 eV, which enables absorption of visible light around 460 nm, and thus various applications in photocatalysis [4,5] and fabrication of solar cells [6]. Nanoscale graphitic carbon nitride has been synthesized as three-dimensional (3D) nanoparticles, two-dimensional (2D) nano-sheets and one-dimensional (1D) chains [7].

Beside PVD and CVD synthetic procedures [1], g-C₃N₄ can be synthesized from simple precursors at a low cost by methods focused on the thermal condensation of nitrogen-rich precursors, such as cyanamide [8], dicyandiamide [9–12], melamine [13–19], cyanuric acid [20] and so forth. The most frequently used synthesis of g-C₃N₄ is based on the thermal condensation of melamine forming melam or melem and consequently melon, which is further condensed to planar structures of g-C₃N₄ [3]. Though melon was firstly synthesized by Liebig [21] in 1834, nowadays there is still ambiguity regarding melon condensation at higher temperatures.

However, the graphitic carbon nitride obtained like this consists of carbon, nitrogen and also minor content of hydrogen, and therefore, the abbreviation g-C_xN_yH_z is more appropriate than commonly used g-C₃N₄. Even in the LiCl and KCl eutectic mixture g-C_{3.0}N_{4.2}H_{0.07} with a very low content of hydrogen was synthesized by Bojdys et al. [12].

Nitrous oxide is one compound of a group of compounds depleting the stratospheric ozone layer and also strongly contributing to the greenhouse effect. Moreover, nitrous oxide persists in the atmosphere for a very long time, approximately 120–150 years. The photocatalytic decomposition of N₂O using semiconductor photocatalysts under UV or Vis irradiation can be one of the promising methods for its removal. Graphitic carbon nitride has been used for the photocatalytic decomposition of NO_x [22] but to the best of our knowledge it has not been used for the decomposition of nitrous oxide yet.

In the literature, the temperatures of the g-C₃N₄ synthesis from melamine are very different, mostly from 450 °C to 700 °C. Therefore, the aim of this work was to synthesize g-C₃N₄ at different temperatures and to provide a comprehensive study of structural, morphological and physico-chemical properties. In addition, all prepared g-C₃N₄ samples were tested for the photocatalytic decomposition of N₂O.

2. Materials and methods

2.1. Chemicals

Melamine of analytical reagent grade was purchased from Sigma-Aldrich (USA). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all solutions. The TiO₂ photocatalyst Evonic P25 was purchased from Precheza (Czech Republic).

2.2. Preparation of g-C₃N₄

The mass of 5 g of melamine was placed into a covered ceramic crucible at room temperature and heated in air in a muffle furnace. The heating temperature was gradually elevated with the heating rate of 20 °C min⁻¹ at a final temperature and kept for 2 h. The final temperatures were 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C and 700 °C. Then, the crucible was cooled to room temperature and a resulting product was ground into powder and characterized by several instrumental methods.

2.3. UV–Vis diffuse reflectance spectroscopy

The UV–Vis diffuse reflectance spectra were recorded with a Shimadzu UV-2600 (IRS-2600Plus) spectrophotometer at room temperature in the range of 220–1400 nm. Reflectance was recalculated to absorbance using the Schuster-Kubelka-Munk's equation as follows

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (1)$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer. The obtained DRS spectra were transformed to the dependencies of $(F(R_{\infty}) \cdot h\nu)^2$ on $h\nu$ in order to obtain transmission energies.

2.4. Photoluminescence spectroscopy

The 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 365 nm. The width of excitation and emission slits was 3 nm.

2.5. Elemental and thermal analysis

The elemental analysis was performed using an elemental analyser CHNS-628 (Leco, USA). Thermogravimetric analysis was performed on a thermal analyser SETSYS-1750 (SETARAM Instrumentation, France) in an alumina crucible and inert atmosphere of argon, the heating rate was 10 °C.min⁻¹. The measurements were performed in the temperature range of 20–900 °C.

2.6. X-ray powder diffraction

The X-ray powder diffraction study was performed using a powder diffractometer INEL CPC 12 (INEL, France) equipped with a curved position-sensitive detector PSD 120 MB/11 (reflection mode, Ge-monochromatized, CuK α ₁ radiation $\lambda = 0.1542$ nm). The diffraction patterns were taken in ambient atmosphere under constant conditions (2000 s, 35 kV, 20 mA). The crystallite size L was calculated according to the Scherrer's equation for broadening $B(2\theta)$ (in radians) at half maximum intensity (FWHM) of a diffraction peak as

$$B(2\theta) = \frac{K\lambda}{L \cos \theta} \quad (2)$$

where λ is the wavelength of the X-rays, θ is the Bragg's angle and K is a constant equal to 0.94 for cube or 0.89 for spherical crystallites. In this study K was rounded to 0.9.

2.7. Fourier transform infrared spectroscopy

The IR spectra were collected by a FT-IR spectrometer Nexus 470 (ThermoScientific, USA) with a DTGS detector using the KBr pellets technique. Exactly 1.0 mg of sample was ground with 200 mg of dried KBr. The pellets were pressed with the pressure corresponding to 8 tons for 30 s under vacuum. The measurement parameters were the following: the spectral region 4000–400 cm⁻¹, the spectral resolution 4 cm⁻¹; 64 scans; the Happ-Genzel apodization. The treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure KBr.

Download English Version:

<https://daneshyari.com/en/article/5448104>

Download Persian Version:

<https://daneshyari.com/article/5448104>

[Daneshyari.com](https://daneshyari.com)