

EXFOLIATED NANOSHEETS OF GRAPHITIC CARBON NITRIDE: STUDY OF STRUCTURE AND MORPHOLOGY

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Abstract

Bulk graphitic carbon nitride (g-C₃N₄) was prepared by heating of melamine at 600 °C for 2 hours. Thermogravimetric analysis showed that this temperature is optimal for the preparation of bulk g-C₃N₄ without unnecessary loss of the material. The characterization was performed by X-ray diffraction (XRD) and scanning (SEM) and transmission electron microscopy (TEM). Specific surface area (SSA) of bulk g-C₃N₄ was about 23 m²g⁻¹. In order to increase the SSA bulk g-C₃N₄ was exfoliated into nanosheets by heating at 500 °C for 4 hours and by ultrasonication in an aqueous dispersion for 1 hour. The SSA increased at 157 m²g⁻¹ by the heating and at 54 m²g⁻¹ by ultrasonication. XRD revealed the layered structure of bulk g-C₃N₄ as well as of both exfoliated g-C₃N₄ samples.

Keywords: Graphitic carbon nitride, exfoliation, nanosheets

1. INTRODUCTION

Graphitic carbon nitride has been considered as a promising material which has been intensively studied during the last decade [1]. This semiconductor material has diamond-like mechanical 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 about 2.7 eV which enables absorption of visible light. Therefore, various applications in photocatalysis [2] and fabrication of solar cells [3] have been investigated.

Beside PVD and CVD synthetic procedures [1] g-C₃N₄ can be prepared from simple precursors by low cost methods based on the thermal condensation of nitrogen-rich precursors, such as cyanamide [4], dicyandiamide [5], melamine [6], cyanuric acid [7] and so forth.

Graphitic C₃N₄ has a layered structure which is potential for formation of graphene-like nanosheets with the thickness of about 2 nm. These nanosheets possess important electronic, thermal, mechanical, optical, catalytic and photocatalytic properties [8-10]. Exfoliation of bulk g-C₃N₄ particles into nanosheets can be done by thermal oxidation, chemical and ultrasonic treatment and by other methods [10]. The aim of this work was to prepare bulk g-C₃N₄ and to study its exfoliation by heating in air and ultrasonication in an aqueous dispersion.

2. EXPERIMENTAL

2.1. Material and chemicals

Melamine of analytical reagent grade was purchased from Sigma Aldrich (USA). Water deionised by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all solutions.

2.2. Exfoliation procedures

Thermal exfoliation was performed by heating at 500 °C in air for 4 hours. The temperature was elevated from room temperature to 500 °C with the heating rate of 20 °C min⁻¹. Ultrasonic exfoliation was performed in an ultrasonic bath for 1 hour. A resulting dispersion was centrifuged at the speed of 3600 min⁻¹ for 20 minutes. Supernatant was filtered through a membrane filter (pores of 0.60 μm). Sediment was dispersed in water, new bulk g-C₃N₄ was added and the procedure was repeated. A filter cake was dried at 110 °C for 2 hours, powdered in a grinding mortar and stored in a reagent flask.

2.2. Thermogravimetric analysis

Thermogravimetric (TG) analysis was performed on a thermal analyzer SETSYS-1750 (SETARAM Instrumentation, France) in an alumina crucible and in the inert atmosphere of argon, the heating rate was of 10 °C.min⁻¹. Measurements were performed in the temperature range of 20-900 °C.

2.3. X-Ray 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, CuKα₁ radiation λ = 0.1542 nm). Diffraction patterns were recorded 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*(2θ) (in radians) at half maximum intensity (FWHM) of a diffraction peak as

$$B(2\theta) = \frac{K\lambda}{L \cos\theta} \quad (1)$$

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

2.4. Specific surface area

Specific surface area of the nanocomposites was measured with an instrument Sorptomatic 1990 (Thermo Electron Corporation, USA) using nitrogen as adsorbing gas and calculated by the Advance Data Processing software according to the BET isotherm at the temperature of 77.3 K and at a ratio *p/p*⁰ up to 0.3, i.e. up to the beginning of capillary condensation.

2.5. SEM and TEM analysis

Scanning electron microscopy was performed using a microscope 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 (Polaron Range SC 7640) by gold in the argon atmosphere.

A transmission electron microscope JEOL 2100 with LaB₆ electron gun was used. Accelerating voltage of 200kV was applied. Images were taken by camera Tengra (EMSIS). For the TEM analysis the samples were prepared by dispersed in ethanol and then sonicated for 5 minutes. One drop of this solution was placed on copper grid with holey carbon film and dried at room temperature.

3. RESULTS AND DISCUSSION

3.1. Preparation and TG analysis

Bulk g-C₃N₄ was prepared by heating of melamine. The heating temperature was chosen based on the TG analysis. As obvious in **Figure 1** the first and highest decrease of mass (about 70 %) was observed in the range of 280-400 °C when sublimation as well as condensation of melamine forming melam and consequently

melem occurred. Melem exists in the temperature range of 400-500 °C and at the higher temperatures up to 600 °C it forms melon. At the temperatures about 600 °C melon further polymerizes to g-C₃N₄ which become unstable at above 650 °C forming some volatile decomposition products [11]. The mass changes are well visible at the TG curve in **Figure 1**. The g-C₃N₄ preparation temperature of 600 C was chosen in order to reach sufficient polymerization of melamine and not to lose g-C₃N₄ by its thermal decomposition.

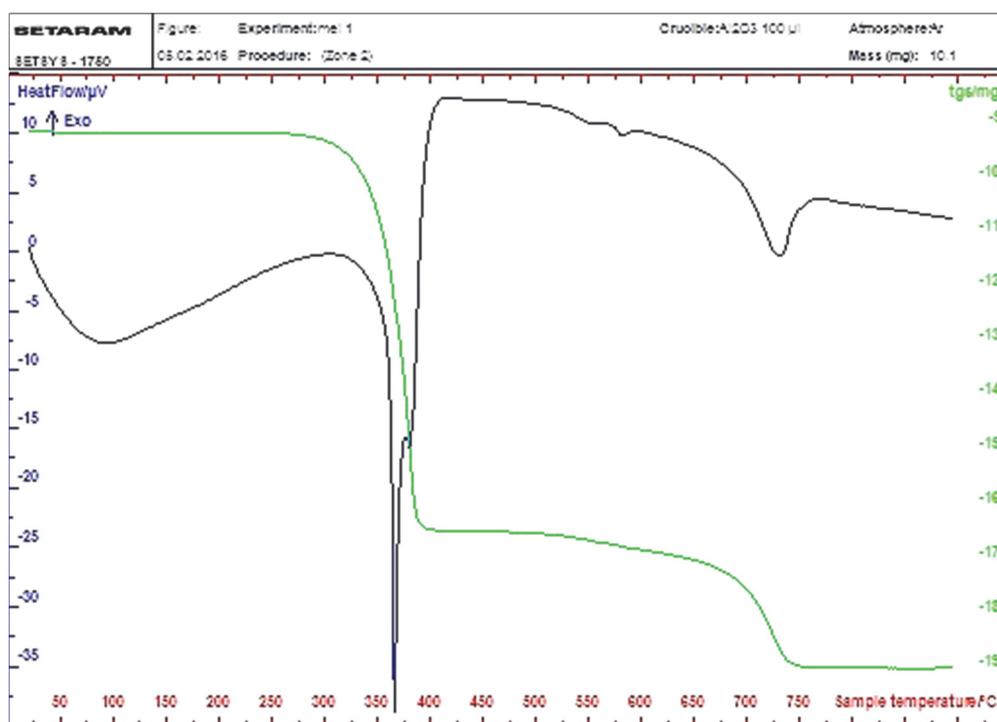


Figure 1 TG curve of heating of melamine

3.2. Characterization of bulk g-C₃N₄

Bulk g-C₃N₄ prepared by annealing at 600 °C of melamine was characterized by XRD (**Figure 2**). The XRD pattern (down) shows two distinct peaks at $2\theta = 12.8^\circ$ and 27.5° , which can be attributed to the hexagonal phase of g-C₃N₄ (JCPDS 87-1526). The strongest peak at $2\theta = 27.5^\circ$ is related to interlayer stacking of the (002) g-C₃N₄ planes. The peak at $2\theta = 12.8^\circ$ is attributed to the (100) planes corresponding to in-plane ordering of the nitrogen-linked heptazine units [12]. The recorded intensity of the (100) peak was low similarly like in works of other authors [13].

The interlayer distance of the (002) planes was calculated according to the Bragg's equation at $d_{002} = 0.36$ nm and the distance between the (100) planes was calculated at $d_{001} = 0.69$ nm. The theoretically calculated distances d_{002} and d_{001} published in literature would be 0.34 nm and 0.73 nm, respectively. The average bulk g-C₃N₄ crystallite size was calculated according to Eq (1) from FWHM of the (002) diffraction peaks at $L = 8.7$ nm.

Morphology of bulk g-C₃N₄ was examined by SEM and TEM (**Figure 3**). The SEM image shows large blocks which consist of 2D g-C₃N₄ nanosheets. In the TEM image, such nanosheets delaminated in ethanol during a sample preparation for the TEM analysis are visible.

The specific surface area of bulk g-C₃N₄ was determined by the BET method at 23 m²g⁻¹. For some applications like catalysis or photocatalysis this magnitude is too low. The exfoliation of bulk g-C₃N₄ into 2D nanosheets can increase the SSA till up to 306 m² g⁻¹ as referred by Niu et al. [8]. Therefore, the next research was focused on the exfoliation of bulk g-C₃N₄.

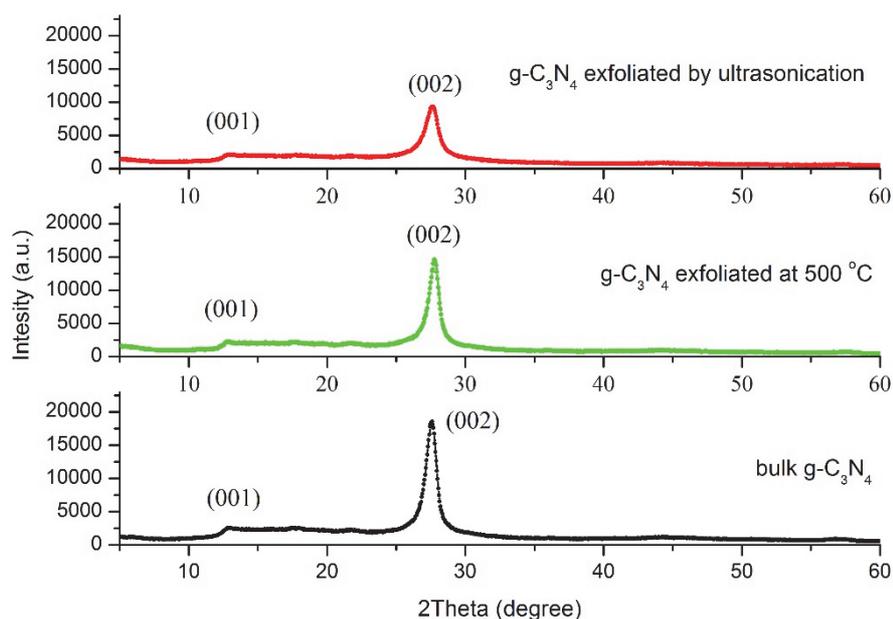


Figure 2 XRD patterns of bulk and exfoliated g-C₃N₄

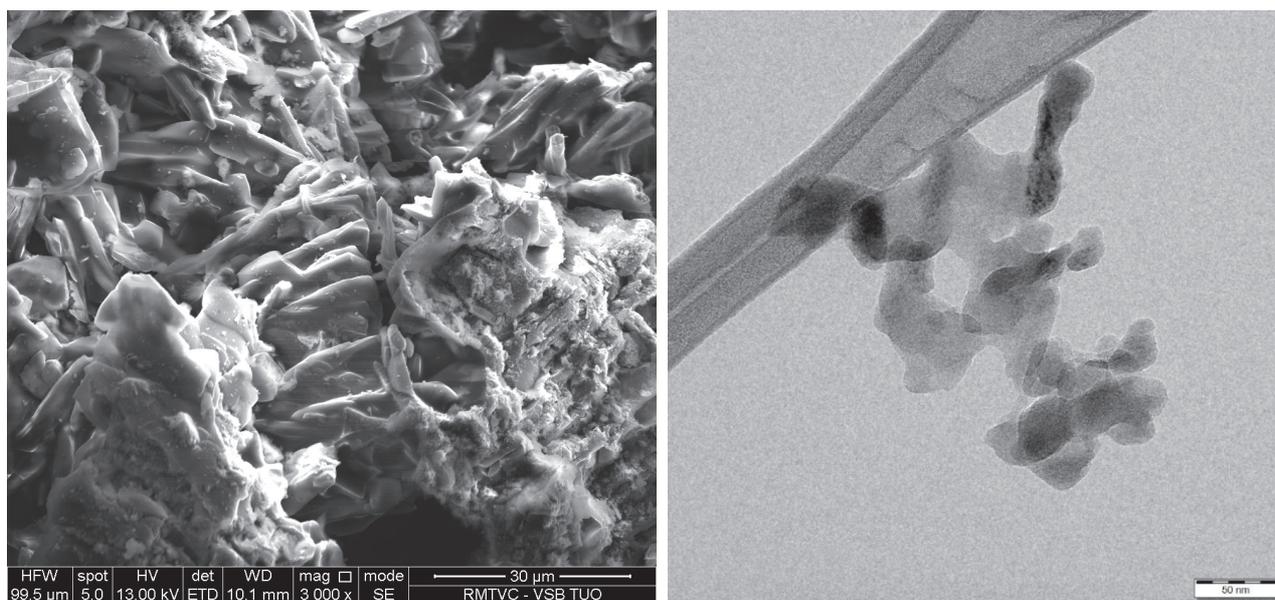


Figure 3 Electron microscopy analysis of bulk g-C₃N₄: SEM image (left) and TEM image

3.3. Exfoliation of bulk g-C₃N₄

Bulk g-C₃N₄ was exfoliated by heating at 500 °C for 4 hours and by ultrasonication of its aqueous dispersion. **Figure 4** shows the UV-VIS spectra of the nanosheets dispersion after ultrasonication. The most significant absorption band around 316 nm indicates the presence of g-C₃N₄ nanosheets composed from 1,3,5-triazine aromatic structures absorbing UV irradiation ($n \rightarrow \pi^*$ transition). Time of ultrasonication was estimated from a plot of absorbances at 316 nm against time of the ultrasonic treatment (**Figure 4**). After 1 hour a majority of bulk g-C₃N₄ was exfoliated into nanosheets, therefore, 1 hour was used for the exfoliation procedure (see Experimental).

The nanosheets were filtered out and the unexfoliated portion was dispersed in water and treated by ultrasound again. This procedure was repeated several times. The separated nanosheets were filtered, dried and powdered.

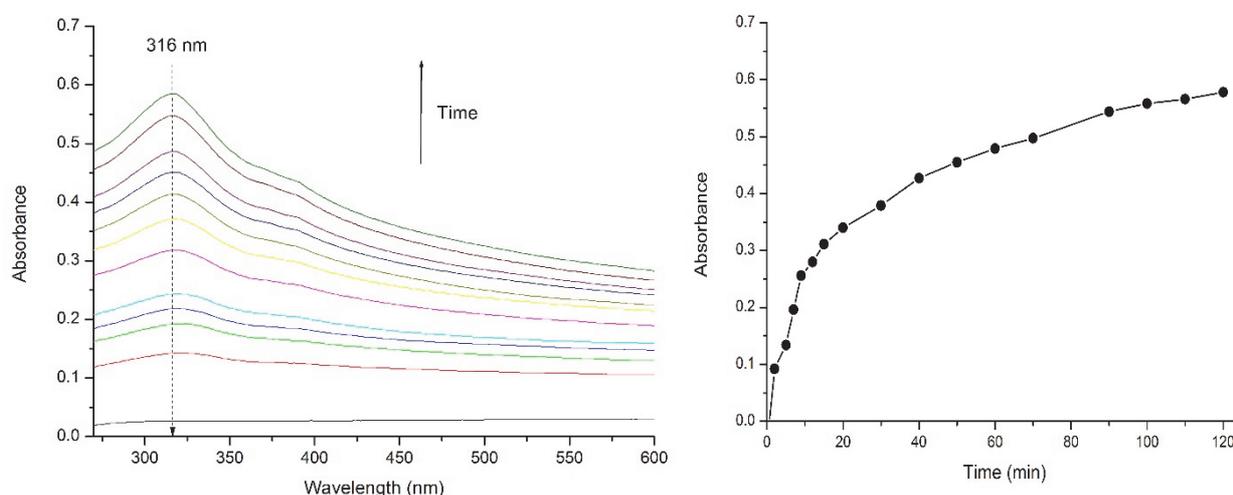


Figure 4 Ultrasonic exfoliation of bulk g-C₃N₄ in aqueous dispersion. Left - UV-VIS spectra of g-C₃N₄ aqueous dispersions at various times of ultrasonication, right - the time dependence of absorbance at 316 nm.

The both exfoliated samples were characterized by XRD (**Figure 2**). Similarly like in case of bulk g-C₃N₄ the diffraction peaks corresponding to the (001) and (002) planes were observed at nearly the same 2θ angles: 12.8° and 27.8° for the sample exfoliated by heating and 12.8° a 27.6° for that exfoliated by ultrasonication. The (002) peaks were used for the calculation of the crystallite sizes: $L = 8.7$ nm and 7.5 nm for the exfoliation by heating at 500 °C and ultrasonication, respectively. It indicates that the exfoliation in liquid dispersions let to formation of smaller crystallites which reassembled during the filtration and drying.

The SSA of the exfoliated samples was measured as well. The sample exfoliated by heating at 500 °C exhibited the value of 157 m² g⁻¹ while the SSA of g-C₃N₄ exfoliated by ultrasound was 54 m² g⁻¹. These facts indicate that the heating at high temperatures was more effective for preparation of g-C₃N₄ nanosheets unless the average crystallite size was substantially changed.

4. CONCLUSION

Bulk g-C₃N₄ was prepared by annealing of melamine at 600 °C for 2 hours and was characterized by XRD, SEM and TEM. The average size of g-C₃N₄ crystallites was estimated according to the the Scherrer's equation at 8.7 nm. The SSA of 23 m²g⁻¹ was determined by the BET method. In order to increase the SSA the exfoliation of bulk g-C₃N₄ was further investigated.

The exfoliation was performed by heating at 500 °C for 4 hours and by ultrasonication in the aqueous dispersion for 1 hour. The process of ultrasonication was monitored by the measurement of absorbances at 316 nm of delaminated g-C₃N₄ nanosheets in dependence on time. The resulting dispersions were filtered, dried and the solid sample was examined by XRD. The self-assembling of the nanosheets into organized layered structures was observed. The average sizes of exfoliated g-C₃N₄ crystallites were estimated at 8.7 nm and 7.5 nm for heating 500 °C and ultrasonication, respectively. Their SSA was determined at 157 m²g⁻¹ and 54 m²g⁻¹, respectively. The heating was found to be the more effective exfoliation procedure than ultrasonication.

In the future research ultrasonification in the presence of nanoparticles and/or other compounds preventing the self-assembling effect will be investigated to obtain heterostructures suitable for photocatalysis.

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