

**THERMAL EXFOLIATION FOR IMPROVING OF THE G-C<sub>3</sub>N<sub>4</sub> PHOTODEGRADATION ACTIVITY**<sup>1</sup>Tomáš RAFAEL, <sup>1,2</sup>Kryštof FONIOK, <sup>1</sup>Vlastimil MATĚJKA<sup>1</sup>VSB - Technical University of Ostrava, Faculty of Materials Science and Technology, Ostrava, Czech Republic, EU, [tomas.rafael.st@vsb.cz](mailto:tomas.rafael.st@vsb.cz), [vlastimil.matejka@vsb.cz](mailto:vlastimil.matejka@vsb.cz)<sup>2</sup>VSB - Technical University of Ostrava, ENET Centre, CEET, Ostrava, Czech Republic, EU, [krystof.foniok@vsb.cz](mailto:krystof.foniok@vsb.cz)<https://doi.org/10.37904/nanocon.2023.4789>**Abstract**

Graphitic carbon nitride is one of the most studied photocatalysts for environmental applications as well as for the production of hydrogen. Its band gap at 2.7 eV means that the photocatalytic activity of this material can be activated with the light of wavelength 460 nm and lower. Thermal polycondensation of suitable precursors, for example melamine, is a widely adopted method of bulk g-C<sub>3</sub>N<sub>4</sub> synthesis. As prepared, bulk g-C<sub>3</sub>N<sub>4</sub> suffers from low photodegradation activity, mainly associated with low specific surface area and high rate of electron-hole recombination. G-C<sub>3</sub>N<sub>4</sub>, similarly to graphite, has a layered structure and to increase the specific surface area, the thermal, chemical, and mechanical exfoliation methods of its layers are adopted. In this work, the effect of holding time at 525 °C during g-C<sub>3</sub>N<sub>4</sub> exfoliation on its photodegradation activity against rhodamine B under irradiation with light of wavelength 420 nm is reported. The effect of holding time on the specific surface area, the structure of the resulted products, the band gap energies, and particle size was also studied. The highest value of specific surface area was achieved for sample exfoliated for 120 min, the highest photodegradation activity was achieved for sample exfoliated for 90 min.

**Keywords:** Photocatalysis, g-C<sub>3</sub>N<sub>4</sub>, exfoliation, characterization**1. INTRODUCTION**

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a well-known photocatalyst that has been intensively studied for photocatalytic purposes [1]. G-C<sub>3</sub>N<sub>4</sub> can be relatively easily prepared by thermal polycondensation of a suitable precursor, such as melamine [2], dicyanamide [3], or urea [4]. Under appropriately chosen calcination conditions, a bulk g-C<sub>3</sub>N<sub>4</sub> is formed, with a layered structure similar to a graphite. Contrary to TiO<sub>2</sub>, which is the most commonly used and studied photocatalyst, graphitic carbon nitride has a lower band gap energy (2.7 eV) and thus light with wavelength equal to or lower than 460 nm (visible part of electromagnetic spectra) is necessary for generation of electron-hole charge carriers. The as-synthesized bulk g-C<sub>3</sub>N<sub>4</sub> usually suffers from low photodegradation activity due to the fast rate of electron-hole recombination and due to a low specific surface area. Approaches to improve photodegradation activity include doping with suitable metal and non-metal elements [5], combining g-C<sub>3</sub>N<sub>4</sub> with other semiconductors such as TiO<sub>2</sub> [6] or ZnO [7].

A very efficient approach to improving the photodegradation activity is the exfoliation of the layered g-C<sub>3</sub>N<sub>4</sub> structure. Using the exfoliation techniques, the specific surface area of g-C<sub>3</sub>N<sub>4</sub> can be enlarged to hundreds of m<sup>2</sup>·g<sup>-1</sup>. The techniques used for thermal exfoliation most often include chemical and thermal procedures. The chemical procedures are based on the action of strong acids, for example, H<sub>2</sub>SO<sub>4</sub> [8] and the ultrasound can be used to intensify the exfoliation process. Using a proper thermal treatment of bulk g-C<sub>3</sub>N<sub>4</sub>, the individual layers are separated due to the thermal etching process [9]. The efforts to synthesize the exfoliated g-C<sub>3</sub>N<sub>4</sub> directly from precursors are reflected in articles published by Lu et al. [10] and Cui et al. [11].

In the presented research, we studied the effect of the time of calcination at 525 °C on the exfoliation of bulk g-C<sub>3</sub>N<sub>4</sub> prepared by thermal polycondensation of melamine. The structure, optical band gap, specific surface area, and photodegradation activity of exfoliated g-C<sub>3</sub>N<sub>4</sub> samples were characterized and used to indicate the effect of calcination time on the exfoliation process.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of the samples

In the first step, bulk g-C<sub>3</sub>N<sub>4</sub> was prepared by thermal polycondensation of the melamine precursor. In a typical procedure, 10 grammes of melamine was placed in a ceramic crucible, which was covered with a ceramic lid. This prepared sample was subjected to 4h calcination at 550 °C in a muffle furnace, the temperature ramp rate was 3°C·min<sup>-1</sup>, after the calcination step, the sample was allowed to cool slowly in a furnace. The resulting bulk g-C<sub>3</sub>N<sub>4</sub> that appeared as a yellow solid cluster was ground to fine powder, and the sample was labelled bulk-gCN.

In the second step, bulk-gCN was subjected to thermal exfoliation at 525 °C. In this process, approximately 0.5 g of bulk g-C<sub>3</sub>N<sub>4</sub> was carefully spread over the bottom of ceramic dish to form homogenous thin layer. Such prepared sample was heated at 525 °C for 30, 60, 90 and 120 min and samples labelled TEX30, TEX60, TEX90 and TEX120 were obtained. Due to the significant weight loss of the material, the exfoliation procedure for each of the temperature was repeated to obtain reasonable amount of sample for its further characterization.

### 2.2 Characterization methods

X-ray diffraction (XRD) analysis was performed using MiniFlex600 theta/2theta diffractometer (Rigaku, Japan) equipped with Co tube ( $\lambda = 1,78897 \text{ \AA}$ ) and a 1D silicon strip D/teX Ultra250 detector. The powder sample was pressed in a rotational holder, the patterns were recorded in the range 10 – 80 °2Theta with step 0.02 °, and scan speed 3 °·min<sup>-1</sup>. The obtained data were visualised using SW Origin 2020b.

Scanning Electron Microscope (SEM) eXPLORER (ASPEX, USA) was used to observe the morphology of bulk-gCN and TEX120 samples. Before the measurement the samples were coated with an Au/Pd film, and the SEM images were obtained using a backscattered electron (BSE) detector.

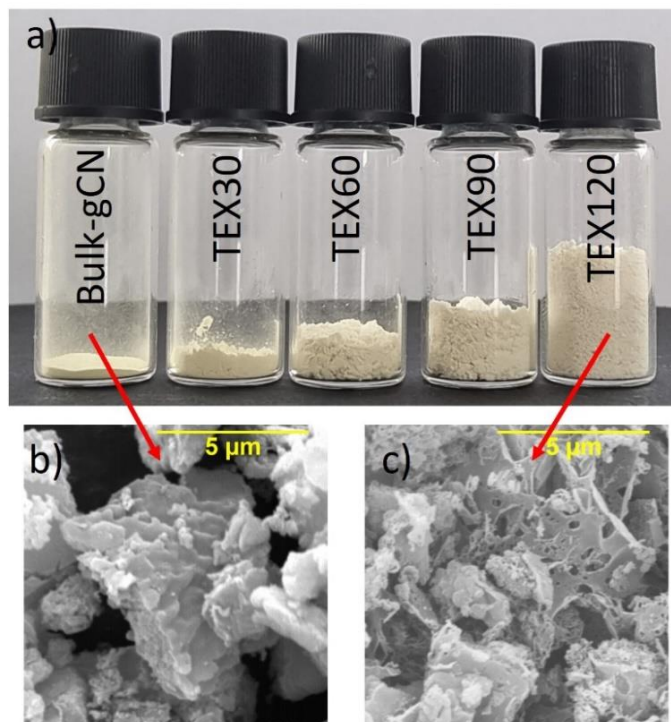
UV-VIS DRS spectra were registered using Shimadzu UV-2600 UV-VIS spectrometer equipped with integrating sphere 2600Plus (Shimadzu Ltd). Powder samples were placed inside a dedicated holder with quartz window and the spectra were recorded at room temperature in the range 200-800 nm. Barium sulphate powder was used for base line registration. Tauc's plots [12] were used to evaluate indirect band gap energies.

The specific surface area of the samples was obtained with the method based on physisorption of nitrogen using an instrument Sorptomatic 1990 (Thermo Scientific, USA). The weight of the samples used for the measurements was about 0.5 g. The data of adsorbed volume of nitrogen was registered in the range of 0.05 – 0.25 of relative pressure. The obtained data were evaluated using Brunauer–Emmett–Teller (BET) method.

The photodegradation activity of the prepared samples was evaluated by photodegradation of Rhodamine B (RhB). In a typical experiment 0.0150 g of sample was weighted into 200 ml glass baker and 150 ml of RhB water solution (5 g·dm<sup>-3</sup>) was added. Such prepared suspension was subjected to irradiation with the light of wavelength 420 nm (FWHM 10 nm) under continuous stirring. In selected time intervals (0 and 120 min) 2ml of suspension was sampled using syringe and further filtered using syringe filter (CHROMAFIL GF/RC-20/25 filters, Macherey-Nagel, Germany) directly to 1 cm microcuvettes made of quartz glass. The absorbance of such collected filtrate was measured at 554 nm using UV-2600 spectrometer (Shimadzu, Japan). The obtained absorbance values at given irradiation time were recalculated to RhB concentration using the method of calibration curve.

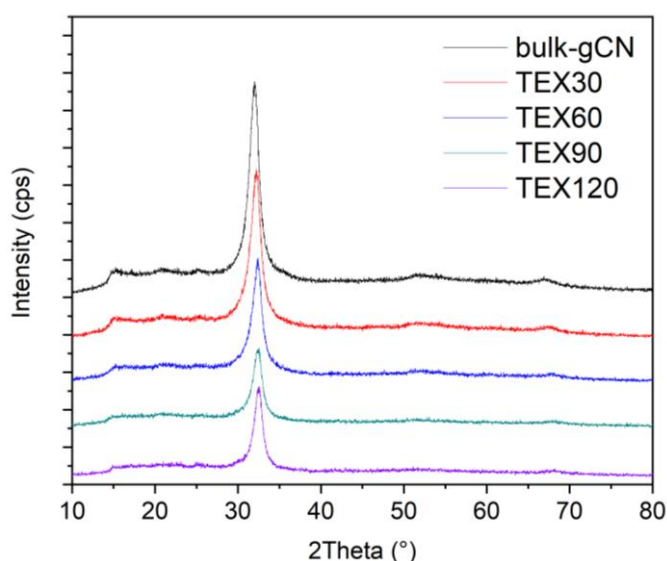
### 3. RESULTS AND DISCUSSION

The appearance of bulk-gCN and exfoliated samples is showed in **Figure 1a**, the morphology of bulk-gCN and exfoliated sample TEX120 is showed in **Figures 1b** and **1c**.



**Figure 1** Appearance of samples bulk-gCN, TEX30, TEX60, TEX90 and TEX120

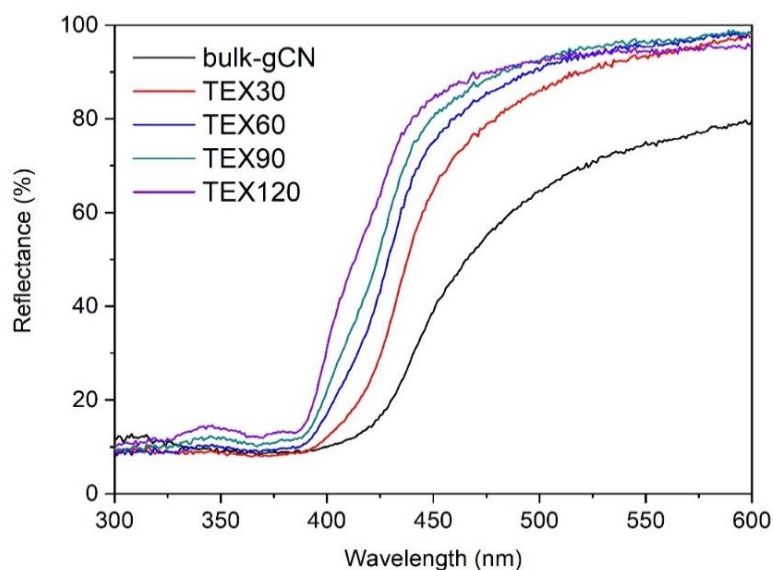
The amount of the samples in vials showed in **Figure 1a** was 40 mg and the images clearly demonstrate the effect of calcination time on character of prepared samples. The higher the calcination time was, the higher the fluffy character of sample was observed. **Figures 1b** and **1c** further demonstrate the difference in morphology of the particles. The particles of bulk-gCN show compact granular character, while the morphology of TEX120 particles shows the presence of exfoliated g-C<sub>3</sub>N<sub>4</sub> sheets with several holes.



**Figure 2** XRD patterns of samples bulk-gCN, TEX30, TEX60, TEX90 and TEX120

Registered XRD patterns for studied samples are compared in **Figure 2**. The most intensive peak observed in diffraction patterns of all samples belongs to reflection from (002) system of planes and is attributed to the interlayer stacking of the conjugated aromatic systems. The maximum position of (001) diffraction line was shifted with time of exfoliation from the value  $32.01^\circ$  observed for bulk-gCN to  $32.45^\circ$  observed for sample TEX120. Such a shift of (002) diffraction line to higher angles is associated with decreased width of g-C<sub>3</sub>N<sub>4</sub> interlayer gallery, i.e. the decreased distance between individual g-C<sub>3</sub>N<sub>4</sub> layers. Comparing the diffraction patterns in **Figure 2**, the decrease of the intensity of (002) diffraction line with the calcination time, is also clearly visible and proves higher exfoliation degree of g-C<sub>3</sub>N<sub>4</sub> with calcination time increasing [13].

Registered UV-VIS DRS spectra of prepared samples are compared in **Figure 3**.



**Figure 3** UV-VIS DRS spectra of prepared samples

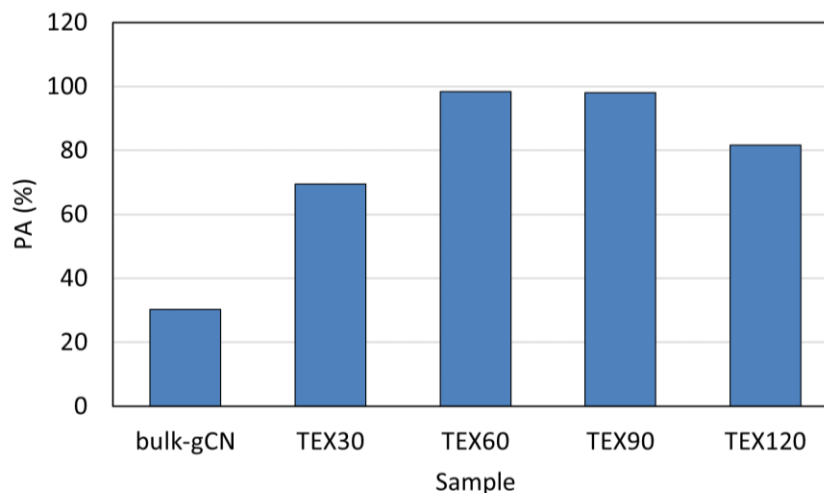
As demonstrated with reflectance spectra of the samples in **Figure 1**, the exfoliation of the samples led to obvious blue shift of the spectra and with the increasing time of exfoliation the blue shift is more pronounced. The blue shift relates to well-known quantum confinement effect typical for nanomaterials. The band gap values obtained using Tauc approach are listed in **Table 1** and prove the shift of values of the band gap energies towards higher values. The wavelength related to given band gap value is also shown in **Table 1**.

**Table 1** The comparison of band gap values, related wavelengths, and values of specific surface area

Sample	E <sub>g</sub> (eV)	λ (nm)	SSA (m <sup>2</sup> ·g <sup>-1</sup> )
bulk-gCN	2.65	464	10
TEX30	2.75	447	52
TEX60	2.80	439	188
TEX90	2.95	417	219
TEX120	2.98	413	255

The values of specific surface area listed in **Table 1** demonstrate significant effect of calcination time on the exfoliation degree, and indirectly indicates the positive effect on g-C<sub>3</sub>N<sub>4</sub> particle size decreasing. The extent of the exfoliation is positively related to particle size and specific surface area and explain the decrease of the values of band gap energies.

Photodegradation activity of the samples after 120 min of irradiation with light of wavelength 420 nm is compared in **Figure 4**.



**Figure 4** Comparison of the photodegradation activity of the prepared samples

**Figure 4** compares the extent of RhB photodegradation and indicates bulk-gCN as the sample with the lowest photodegradation activity. The highest photodegradation activity was observed for the sample TEX60, comparable activity was determined for the sample TEX90. The photodegradation activity of the samples is positively related to the specific surface area in the case of the samples TEX30 and TEX60. Further increase in the calcination time led to a decrease in photodegradation activity although the specific surface area values of the samples TEX90 and TEX120 were significantly increased (compare the SSA values in **Table 1**). This fact can be attributed to the increase of the band gap energy at the TEX90 samples, and especially in the case of TEX120, above the value 2.93 eV which corresponds to the light of wavelength 420 nm, what was the wavelength of the LED source used for the photodegradation test.

#### 4. CONCLUSIONS

The effect of time during thermal exfoliation of bulk-gCN at 525 °C on the morphology of its particles, structure, optical band gap, specific surface area, and photodegradation activity was studied. The data obtained showed a strong effect of exfoliation time on the extent of disintegration of the layered structure. The exfoliated g-C<sub>3</sub>N<sub>4</sub> particles exhibit a fluffy character and the values of the optical band gap increase with the time of thermal treatment. The highest photodegradation activity reached g-C<sub>3</sub>N<sub>4</sub> exfoliated for 60 min, slightly lower value showed the sample with an exfoliation time of 90 min. The decrease of photodegradation activity in the case of sample TEX120, which is the sample with the highest specific surface area, was observed and was related to the increase of band gap energy. Further tests with the light source with wavelength 410 nm and lower have to be performed to describe the discrepancy between the specific surface area and photodegradation activity of a such highly exfoliated g-C<sub>3</sub>N<sub>4</sub> samples which band gap energies are significantly shifted towards higher energies.

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