THERMAL STABILITY OF g-C_3N_4 IN THE PRESENCE OF SELECTED OXIDES

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Abstract

Graphitic carbon nitride (g-C_3N_4) is an intensively studied photocatalyst active in the visible spectrum range. The most commonly used method for g-C_3N_4 preparation is the thermal polycondensation of melamine at temperatures in the range of 500–600°C, resulting in the so-called bulk g-C_3N_4. Such prepared g-C_3N_4 suffers from low photodegradation activity, mainly due to its low specific surface area and fast e^-/h^+ charge carriers recombination. One way to suppress electron-hole recombination is to prepare composite materials in which g-C_3N_4 is combined with another semiconductor, such as TiO_2, and ZnO. These composites are often prepared from individual components by their mechanical mixing followed by heat-treatment of the prepared mixture. This paper focuses on the study of the thermal stability of g-C_3N_4 in the presence of TiO_2, Fe_2O_3, ZnO, SiO_2, and Al_2O_3. The prepared mixtures of g-C_3N_4 with the corresponding oxide phase were subjected to simultaneous thermal analysis at temperatures up to 1000°C, and also heated in a muffle furnace at 400, 450, and 500°C. The results indicate the negative effect of TiO_2 and Fe_2O_3 on the thermal stability of g-C_3N_4, while ZnO, SiO_2, and Al_2O_3 did not show this effect.

Keywords: g-C_3N_4, composites, thermal stability, characterization

1. INTRODUCTION

Graphitic carbon nitride is a widely studied material for photocatalytic applications. The advantage of g-C_3N_4 over the most often used TiO_2 photocatalyst is its narrower band gap, reaching an energy of 2.7 eV [1]. This value indicates that g-C_3N_4 is an active photocatalyst in the visible light spectrum, specifically under irradiation with wavelengths of 460 nm and shorter. The most common method for g-C_3N_4 synthesis is based on the thermal polycondensation of a suitable precursor, resulting in the so-called bulk g-C_3N_4. Melamine, urea, or dicyandiamide are the most common precursors used for this purpose [2-4]. The thermal polymerization of the precursors occurs most often in the temperature range of 500 – 600 °C, and thus, the final g-C_3N_4 is considered thermally stable at these temperatures.

As synthesized bulk g-C_3N_4 suffers from low specific surface area and fast recombination of e^-/h^+ charge carriers, which negatively influences the photodegradation activity of bulk g-C_3N_4. Several approaches have been adopted to overcome this disadvantage. Thermal, chemical, or mechanical exfoliation processes [5] are used to increase the specific surface area of g-C_3N_4. The specific surface area (SSA) of original bulk g-C_3N_4 typically reaches values up to 10 $m^2 \cdot g^{-1}$, and using the exfoliation process, SSA values even higher than 300 $m^2 \cdot g^{-1}$ were reported. To suppress the electron-hole recombination rate, various approaches of the g-C_3N_4 modification have been adopted. The doping of g-C_3N_4 with metallic and non-metallic elements [6], and its combination with other semiconductors [7], or inert matrices [8], is frequently used.

Preparation of the composites could also bring other positive effects, as was reported, for example, by Matějka et al. [9] for composites kaolinite/TiO_2. In the case of g-C_3N_4, reported composites include for example g-C_3N_4/TiO_2 [10], g-C_3N_4/ZnO [11], g-C_3N_4/Fe_2O_3 [12], g-C_3N_4/SiO_2 [13], or g-C_3N_4/Al_2O_3 [14]. The synthesis procedures for the composites mentioned above include also the thermal treatment of g-C_3N_4 mixtures with

selected oxides. As reported in papers [11-14], in the case of g-C_3N_4/TiO_2 the temperature was 500 °C, g-C_3N_4/ZnO the temperature range was 80 - 100 °C, g-C_3N_4/Fe_2O_3 the temperature was 500 °C, g-C_3N_4/SiO_2 the temperature was 450 °C, and g-C_3N_4/Al_2O_3 the temperature was 550 °C. All the reported temperatures are within the range where the studied oxides, as well as g-C_3N_4, are considered stable.

In our work, we focused on evaluating the thermal stability of the composites g-C_3N_4/TiO_2, g-C_3N_4/ZnO, g-C_3N_4/Fe_2O_3, g-C_3N_4/SiO_2, and g-C_3N_4/Al_2O_3 prepared by mechanical homogenization of individual components. Such prepared composites were subjected to TG analysis to address their weight stability during heating. The mechanical mixtures were also subjected to thermal treatment at 400, 450, and 500 °C. The composites before and after thermal treatment were subjected to elemental analysis and X-ray diffraction studies.

2. EXPERIMENTAL

2.1 Sample preparation

Bulk g-C_3N_4 was prepared by thermal polycondensation of melamine precursor. In a typical procedure, 10 grams of melamine was put into a ceramic crucible, which was covered with a ceramic lid and calcined for 4h at 550 °C in a muffle furnace. After the calcination step, the sample was allowed to cool down slowly in a furnace. The resulting bulk g-C_3N_4 was labelled as gCN.

TiO_2 was prepared by thermal hydrolysis of $TiOSO_4$ (Precheza, Czech Republic). ZnO was purchased from (P-lab, Czech Republic), Fe_2O_3 was supplied by (Precheza, Czech Republic), SiO_2 and Al_2O_3 were obtained from (Průmyslová keramika, Czech Republic).

The composites were prepared by mechanical mixing of individual components in a weight ratio 1:1. The planetary ball mill PM100 (Retsch, Germany) was used for this purpose. The homogenization was conducted for 10 minutes at 450 rpm using a 250 mL stainless steel vessel. The resulting samples were labeled gCN/Me_xO_y, where Me_xO_y is given oxide.

Obtained mechanical mixtures were weighed into a ceramic crucible and thermally treated for 60 min at the temperatures 400, 450, and 500 °C, in a muffle furnace LE 05/11 (LAC, Czech Republic) with a temperature ramp-rate 5°C·min^{-1}. The resulting samples were assigned as gCN/Me_xO_y-T, where Me_xO_y represents given oxide, and T temperature of thermal treatment.

2.2 Sample characterization

Thermogravimetry was carried out on a simultaneous thermal analyzer, SDT 650 TA Instruments, USA, which has a DSC/TGA system with a horizontal dual-beam design for heat flow and weight measurements. Each sample (~ 20 mg) was inserted into α-Al_2O_3 crucible and heated up to 1000 °C (5°C·min^{-1}) in a dynamic air atmosphere. The crucibles were covered with α-Al_2O_3 lid during the experiments.

The carbon, hydrogen, and nitrogen content of the prepared samples was determined using the instrument LECO 828 (LECO, USA). Typically, around 100 mg of sample was loaded in a tin foil. In the next step, the tin foil with the sample was gently squeezed, the prepared sample was loaded into an autosampler, and the analysis proceeded in automatic mode. EDTA was used for calibration.

X-ray diffraction (XRD) analysis was performed using MiniFlex600 theta/2theta diffractometer (Rigaku, Japan) equipped with a Co tube (λ = 1,78897 Å) 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 a step of 0.02 °, and a scan speed of 5 °·min^{-1}. The obtained data were evaluated using SmartLab Sudio II (Rigaku, Japan) and further visualised using SW Origin 2019.

3. RESULTS AND DISCUSSION

Weight loss of the individual composites after thermal treatment at selected temperatures is graphically depicted in **Figure 1a**. All of the samples show growing weight loss with increased temperature. Within the tested composites, the composites gCN/Fe_2O_3 and gCN/TiO_2 show significantly higher weight loss, reaching approx. 50 % after one hour long calcination at 500 °C. The other three composites, i.e., gCN/ZnO, gCN/SiO_2, and gCN/Al_2O_3, show the weight loss after the same conditions up to 20 %. This observation highlights the fact that some of the chemicals could accelerate the decomposition of gCN, namely TiO_2 and Fe_2O_3.

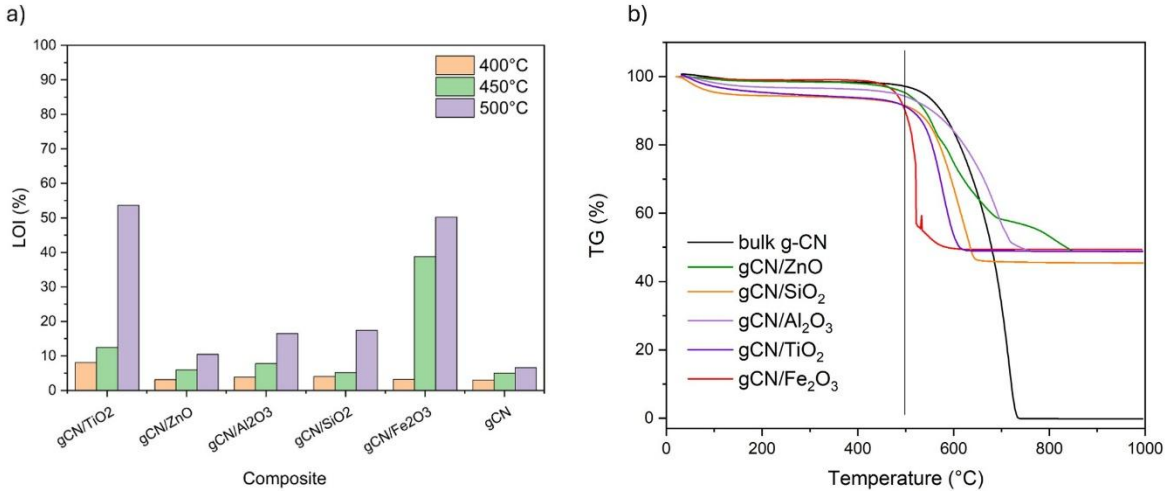

Figure 1 a) Loss on ignition of the composites at given temperatures, **b)** TG curves registered for the composites

The TG curves registered for the prepared composites are compared with TG registered for gCN in **Figure 1 b**. The run of the TG curve registered for pure gCN indicates the highest thermal stability of this sample. On-set temperature of gCN degradation is shifted to a higher temperature, and the whole decomposition process of this sample finishes at 730 °C and TG curve showed 100 % of weight loss. As expected, the maximum weight loss registered for the composites reached approximately 50 %. Comparing the TG curves, the composite gCN/Fe_2O_3 shows the least thermal stability followed by gCN/TiO_2, gCN/SiO_2, gCN/ZnO, and gCN/Al_2O_3. This ranking reflects the onset temperature of weight loss and steepness of individual TG curves. TG curve of gCN/ZnO shows two distinguishable zones of weight loss, and the complete decomposition of gCN (the maximum weight loss) occurred at 840 °C, which is the highest temperature compared to other composites.

The composites after their thermal treatment in a muffle furnace at selected temperatures were subjected to the analysis of carbon, nitrogen, and hydrogen, and the results are compared in **Table 1**.

Table 1 Content of carbon, hydrogen, and nitrogen in the studied samples

Samples	C (wt.%)				H (wt.%)				N (wt.%)			
	Orig	400	450	500	Orig	400	450	500	Orig	400	450	500
gCN	35.3	-	-	-	1.82	-	-	-	59.5	-	-	-
gCN/TiO_2	19.6	19.9	19.2	3.95	1.63	1.11	1.16	0.485	31.7	32.7	31.0	7.08
gCN/Fe_2O_3	19.1	18.5	6.68	0	0.808	0.788	0.336	0	30.4	29.5	11.2	0
gCN/ZnO	18.8	18.4	17.8	17.3	0.882	0.810	0.778	0.695	30.3	29.7	28.8	28.0
gCN/SiO_2	18.5	-	-	17.4	1.36	-	-	0.983	30.4	-	-	28.0
gCN/Al_2O_3	18.6	-	-	15.9	1.11	-	-	0.806	29.7	-	-	25.6

As evident from **Table 1**, all the composites show a decrease in carbon, hydrogen, and nitrogen content with growing calcination temperature. The complete decomposition of gCN was observed in the case of composite gCN/Fe_2O_3 calcined for 60 min at 500 °C, the analyzed C, H, and N contents reached 0 wt.%. The second most pronounced decrease in C, H, N contents shows composite gCN/TiO_2 after its 60 min long thermal treatment at 500 °C. After 60 min long calcination at 500 °C, the composites gCN/ZnO, and gCN/SiO_2 showed a decrease in carbon content, reaching approximately 1 wt.% and these composites are thermally stable up to 500 °C. These results are in good agreement with the registered yields shown in **Figure 1a**.

The phase composition of the original and calcined composites was studied using the XRD method, and the registered diffraction patterns are shown in **Figure 2.**

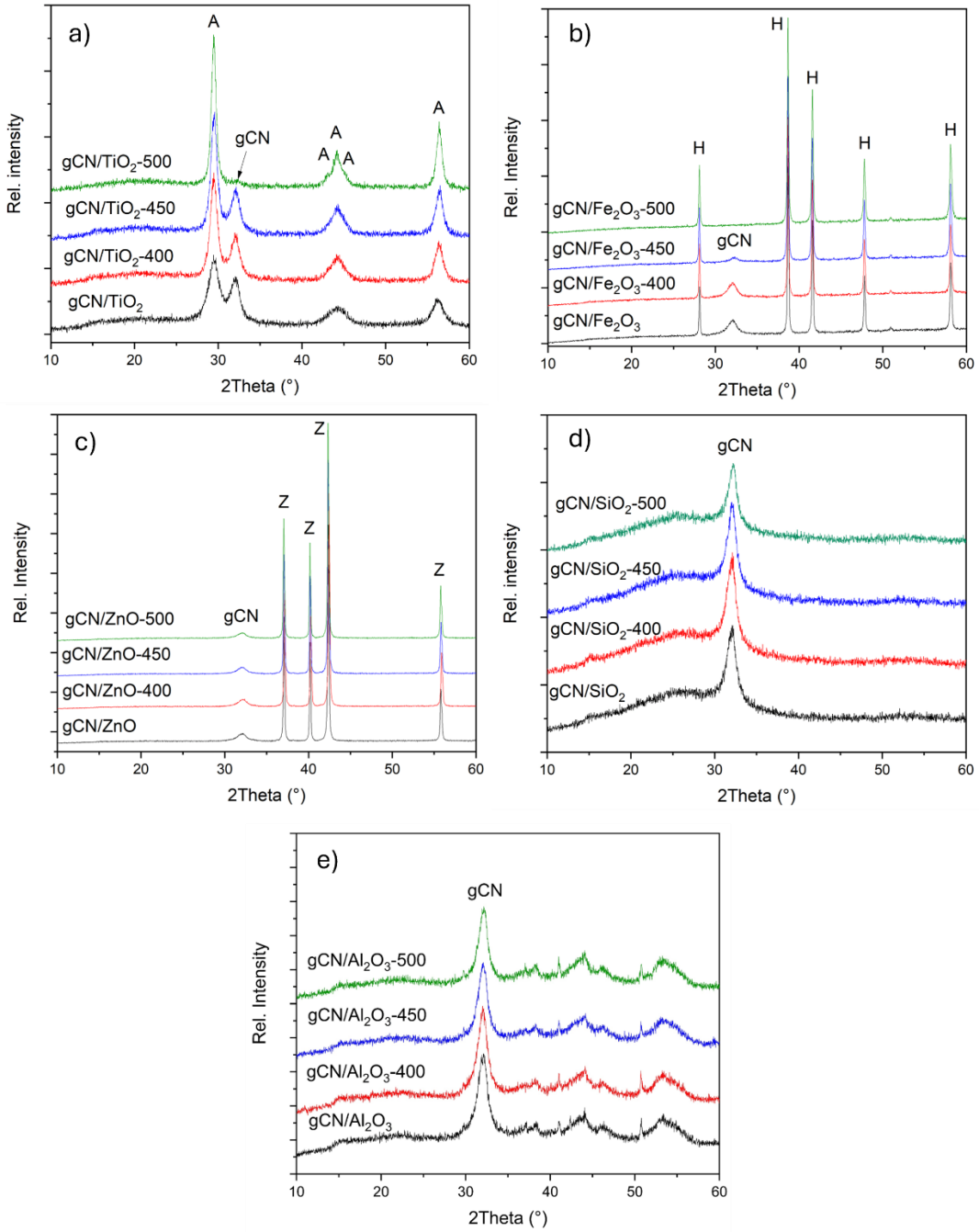

Figure 2 X-ray diffraction patterns of a) gCN/TiO_2, b) gCN/Fe_2O_3, c) gCN/ZnO, d) gCN/SiO_2, and e) gCN/Al_2O_3 composites

X-ray diffraction patterns confirmed and supported the findings about the stability of the composites obtained during the LOI tests and elemental analysis. The X-ray diffraction patterns of gCN/TiO_2 and gCN/Fe_2O_3 composites are shown in Figures 1a-b. In the case of gCN/Fe_2O_3 the significant reduction in the intensity of (002) diffraction peak of gCN occurred already at 450°C, while for gCN/TiO_2 the significant reduction was indicated at temperature 500 °C. The other composites did not show a decrease in the intensity of this diffraction line even after 60 min long treatment at a temperature of 500 °C.

4. CONCLUSION

The stability of the composites of bulk g-C_3N_4 with selected oxides was studied. It was observed that the stability of g-C3N4 was not affected by ZnO, Al_2O_3, and SiO_2, while its thermal stability was significantly decreased in the presence of TiO_2 and Fe_2O_3. The mechanism of the g-C_3N_4 decomposition over these oxides has to be further investigated.

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DATA AVAILABILITY

The dataset is available in repository Zenodo: 10.5281/ZENODO.17348206.

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