COMPOSITES BASED ON EXFOLIATED g-C$_3$N$_4$ AND TiO$_2$

[1]Kryštof FONIOK, [1,2]Aneta SMÝKALOVÁ, [3]Petra MATĚJKOVÁ, [1,2]Petr PRAUS,
[1,2]Vlastimil MATĚJKA

[1]*VSB - Technical University of Ostrava, FMST, Department of Chemistry, Ostrava,*
Czech Republic, EU, krystof.foniok@vsb.cz

[2]*VSB - Technical University of Ostrava, Institute of Environmental Technology, Ostrava,*
Czech Republic, EU, petr.praus@vsb.cz

[3]*VSB - Technical University of Ostrava, Center of Advanced Innovation Technologies, Ostrava,*
Czech Republic, EU, petra.matejkova@vsb.cz

Abstract

The photocatalytic degradation of dangerous substances is widely studied topic and many scientific reports have been already published about this issue. Undoubtedly, titanium dioxide is the most often studied compound for photocatalysis in UV region, while graphitic carbon nitride is the most often studied photocatalyst in VIS region. Combination of the photocatalysts leads to the formation of composites with improved photocatalytic performance and better applicability. In this work, the composites of exfoliated g-C$_3$N$_4$ and TiO$_2$ in anatase form were prepared by mechanical mixing of both components in weight ratio 1:1. The prepared mechanical mixtures as well as the original components were thermally treated at 300 a 400 °C and characterized using X-ray diffraction method, infrared (FTIR) spectroscopy, UV-VIS diffuse reflectance spectroscopy (DRS). The morphology of the particles was studied using scanning electron microscopy (SEM). The photocatalytic activity of the samples was tested using the method based on the 2h long UV assisted photodegradation of Acid Orange 7. The results indicated the highest photodegradation activity for a non-thermally treated mechanical mixture of g-C$_3$N$_4$ and TiO$_2$. For the composites the photocatalytic activity (PA) decreases with the temperature of the thermal treatment, the same effect was observed for original TiO$_2$, while for original g-C$_3$N$_4$ the photodegradation activity increased with the temperature of the treatment.

Keywords: Photocatalysis, g-C$_3$N$_4$, TiO$_2$, composites, properties

1. INTRODUCTION

The photacatalysts based on g-C$_3$N$_4$ has attracted the attention of the scientific community mainly due to their photodegradation activity in VIS region. Although several synthesis procedures of g-C$_3$N$_4$ have been reported the process based on thermal polymerization of melamine is used most often and g-C$_3$N$_4$ in the so called bulk structure is obtained [1]. The process of the melamine thermal treatment has to be carefully controlled other way the products with different photodegradation activity are obtained [2]. Bulk g-C$_3$N$_4$ suffers from low photoacatalytic efficiency attributed mainly to low specific surface area and fast recombination of charge carriers. Exfoliation of the bulk g-C$_3$N$_4$ structure leads to the separation of the individual layers and significant increase of photocatalytic activity. The exfoliation procedures include for example the thermal treatment [3], sonication [4] or chemical treatment [5]. Other approach to improve the photodegradation activity is the doping of the g-C$_3$N$_4$ with metal and non-metal elements [6] or the combination of the bulk g-C$_3$N$_4$ with other photocatalyst for example with BiOIO$_3$ [7], TiO$_2$ [8], graphene oxide [9] etc.

Tropová et al. [1] prepared the composites using the thermal treatment of bulk g-C$_3$N$_4$ with TiO$_2$ (in anatase form) at 300 °C and tested the photodegradation activity of the prepared samples against the N$_2$O. The highest photodegradation efficiency was observed for the composite with weight ratio of TiO$_2$:g-C$_3$N$_4$ 1:3. Liu et al prepared the composite of g-C$_3$N$_4$/TiO$_2$ by the calcination of TiO$_2$ Degussa P25 with urea in different weight

ratios. The photoactivity of prepared samples were tested using VIS light assisted photodegradation of formaldehyde.

The aim of our work was to prepare the composite of the exfoliated graphitic carbon nitride with titanium dioxide, characterization of the prepared samples by X-ray diffraction method, infrared spectroscopy and UV-VIS DRS spectroscopy. The morphology of the prepared samples was studied by scanning electron microscopy. Photocatalytic activity of the prepared samples was tested by the photodegradation of the model azo dye acid orange 7.

2. MATERIALS AND METHODS

The exfoliated graphitic carbon nitride was prepared using two steps procedure. In the first step, the so called bulk g-C_3N_4 was prepared by the thermal poly-condensation of melamine in a muffle furnace. In detail, 10g of melamine was weighted in a ceramic crucible, which was then covered with a ceramic lid. The crucible was heated with 3 °C·min^{-1} to the final temperature 550 °C and held 4h at this temperature. In the second step, the bulk g-C_3N_4 was crushed in agate mortar and put in a thin layer on ceramic plate and heated in a muffle furnace at 500 °C for 2h and then fast cooled and the sample of exfoliated g-C_3N_4 assigned as Tex was obtained. The composite g-C_3N_4/TiO_2 was prepared by mechanical mixing of Tex and TiO_2 (anatase form) in an agate mortar in weight ratio 1:1. The obtained mechanical mixture was split in a three equivalent portions while two of them were 2h thermally treated at 300 and 400 °C, respectively and composites 1:1-300 and 1:1-400 were obtained. Initial Tex and TiO_2 were thermally treated at the same conditions as 1:1 mixture and the samples were labeled as Tex-300, Tex-400, TiO_2-300 and TiO_2-400 were obtained.

All the samples were characterized using X-ray diffraction technique on powder diffractometer Miniflex 600 (Rigaku) equipped with Co tube (40kV, 15mA) and 1D detector D-Tex. X-ray powder diffraction patterns were registered in the range 10 - 90 °2Theta.

Infrared spectra of the samples were registered in ATR mode using Fast Fourier infrared spectrometer Nicolet iS50 equipped with ATR diamond crystal. The spectra were registered in the range 4000 - 450 cm^{-1} and 32 spectra were averaged.

UV-VIS diffuse reflectance spectra were measured using UV-VIS spectrometer UV-2600 (Shimadzu) equipped with integrating sphere IRS-2600Plus (Shimadzu). The spectra were registered in the range 220 - 800 nm. The diffuse reflectance data were further transformed using Kubelka-Munk function and Tauc's plots was used for the evaluation of indirect band gap energies.

The morphology of the particles of the composite 1:1 was studied using scanning electron microscope Aspex Explorer 4 (ThermoScientific) equipped back scattered electron detector. To prepare the samples for SEM investigation the diluted suspension of the powder sample in ethanol was spread over an aluminum pin and let dry at the laboratory temperature.

Photodegradation activity of the samples was evaluated using the method based on the UV assisted photodegradation of azo dye acid orange 7 (AO7). In a typical experiment, 0.0500 g of the sample was put to the glass bowl with 150 ml of distilled water and homogenized on the electromagnetic stirrer at 250 rpm. After this step 15 ml of the AO7 solution (c = 7.136·10-4 mol·dm^{-3}) was added to the stirred suspension.So prepared stirred suspension was covered and after 30 min of stirring in the dark 2 ml of suspension was sampled using syringe and filtered using a syringe filter Chromafil PP/GF/RC-20/25. The absorbance of the filtered solution at 480 nm was measured using HELIOS Σ spectrometer (ThermoSpectronic) to obtain the absorbance value A_0. After this step the stirred suspension was irradiated using UV light ((BLB 36 W, NARVA) for 120 min. After this period, 2 ml of the suspension was sampled, filtered and absorbance A_{120} was measured. The measured values of the absorbance were transformed to concentration values c_0 and c_{120} and the ratio c_{120} / c_0 was used for the comparison of the photodegradation activity of the individual samples.

3. RESULTS AND DISCUSSION

The SEM image demonstrating the morphology of the 1:1 composite is shown in **Figure 1**. The strong agglomeration of the g-C_3N_4 flakes was observed, TiO_2 particles were homogenously distributed over the surface of the g-C_3N_4 particles.
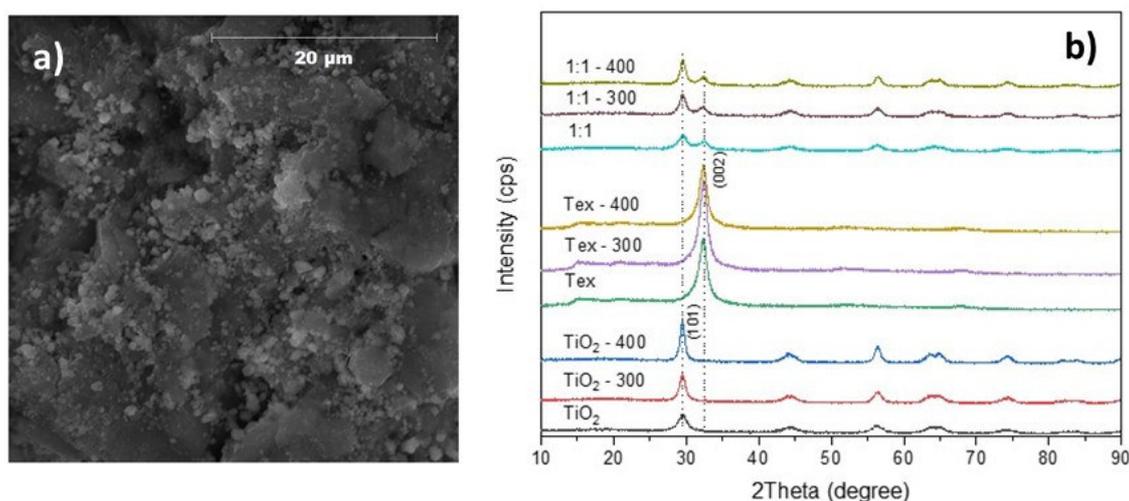
Figure 1 a) SEM image of the particles of the composite 1:1, b) X-ray powder diffraction patterns of the studied samples

The registered X-ray diffraction patterns are shown in **Figure 1b**. The X-ray diffraction technique revealed that the samples in TiO_2 series were composed of anatase as a sole phase as well as the samples in Tex series were composed of g-C_3N_4, no impurities were detected by the X-ray diffraction method in the samples in both series. Comparing the profiles of the (101) diffraction peak of anatase the increasing of the intensity and sharpening of this peak with temperature was observed. This fact demonstrates the growing of the anatase crystallite size with temperature. The X-ray diffraction patterns of Tex were not affected by its thermal treatment as evident from **Figure 2** what reflects the fact that the Tex sample had been already subjected to higher temperatures (550 and 500 °C, respectively) during its preparation and thus its treatment at the temperatures 300 and 400 °C did not influence its structure. The run of the diffraction patterns registered for the composites 1:1 reflects the behavior of the individual components TiO_2 and Tex discussed above.

An example of Tauc´s plot for the non-thermally treated samples is shown in **Figure 2**. Band gap energies evaluated from the Tauc´s plot for all of the studied samples are listed in **Table 1**. The run of the curves obtained for the original non-thermally treated TiO_2 and Tex (**Figure 2a**) indicate the monophase composition and the estimated values of the band gaps listed in Table 1 represent the typical values for both TiO_2 and g-C_3N_4. The same situation is for the samples TiO_2-400 and Tex-400 (**Figure 2b**). The separation of two curves belonging to both components in the case of composite 1:1-400 (**Figure 2b**) is more distinct in comparison to the composite 1:1 (**Figure 2a**). Comparing the values listed in **Table 1** it is observable that the band gap energy (E_g) values for TiO_2 decreased with the temperature contrary to the trend observed for Tex for which the E_g values increased with the temperature. The decreasing of the E_g value for TiO_2 can be related to the growing of the crystallite at the elevated temperatures, while the growing of E_g values with temperature observed for Tex could be related to more effective separation of the individual layers of Tex particles due to the additional exfoliation of its structure. In the case of the composites the completely opposite trend of E_g values for both components was observed, the estimated values for TiO_2 grows with the temperature while the E_g values estimated for Tex decrease with the temperature. This fact signalizes the interaction between both components resulting in different optical properties of the composites in comparison to the pristine materials.

Table 1 Band gap energies of the studied semiconductors and their composites

Sample	E_g (eV)	Sample	E_g (eV)	Sample	E_g (eV)
TiO₂	3.32	Tex	2.68	1:1	2.68/3.06
TiO₂-300	3.29	Tex-300	2.72	1:1-300	2.65/3.13
TiO₂-400	3.29	Tex-400	2.74	1:1-400	2.64/3.16
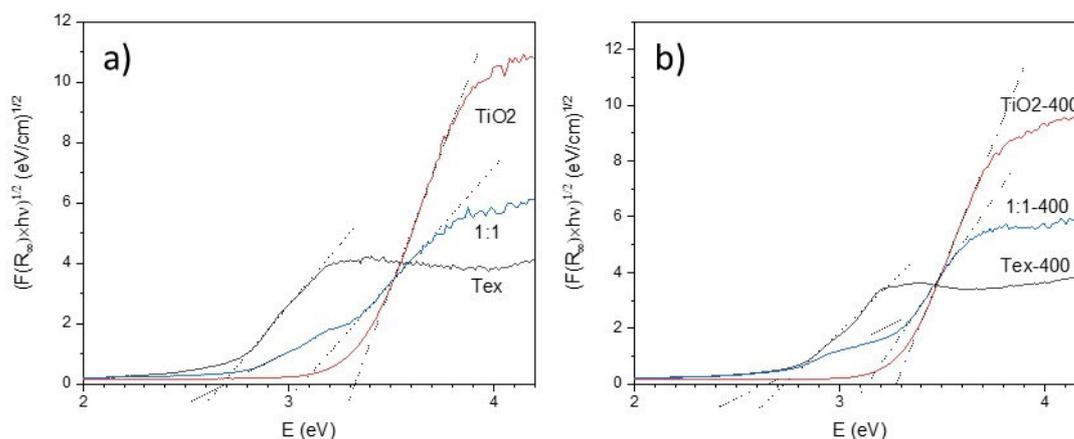
Figure 2 Tauc´s plot for the a) original components TiO₂ and Tex and mechanical mixture 1:1
and b) samples thermally treated at 400 °C
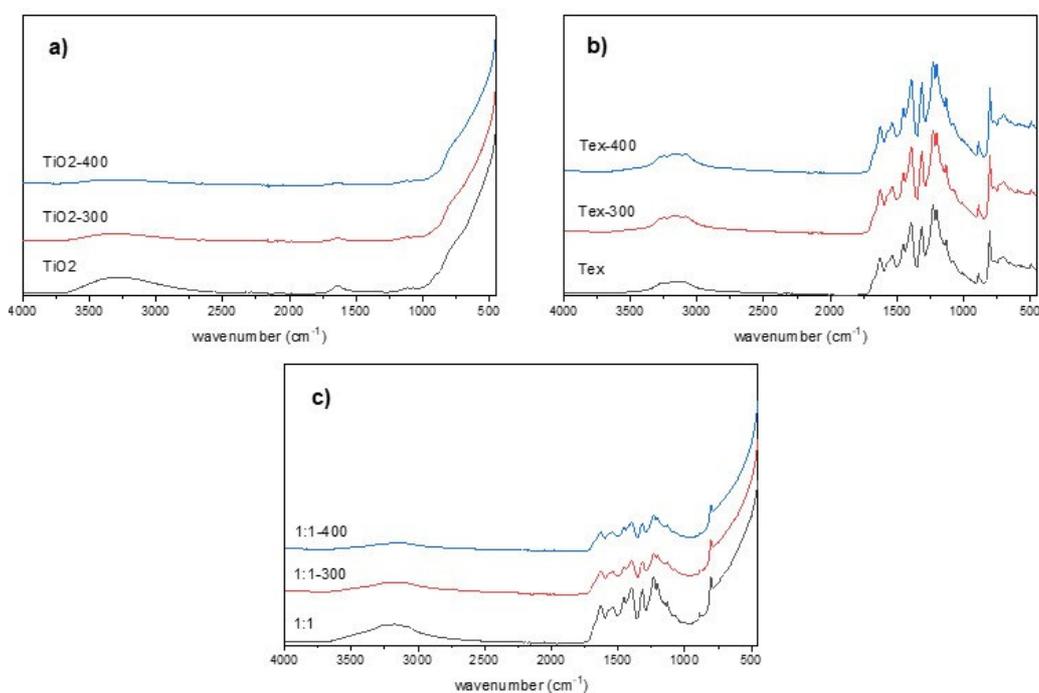
Figure 3 IR spectra of the studied samples (a) TiO₂, (b) Tex and (c) 1:1 composites

FTIR spectra of TiO₂ samples are shown in **Figure 3a**. The increase in the values of IR absorption in the region bellow 1000 cm⁻¹ is attributed to the Ti-O stretching modes of anatase. Bands in the regions 3000-3800 cm⁻¹ and 1500-1700 cm⁻¹ are ascribed to stretching and bending vibrations of O-H groups and demonstrate the

presence of adsorbed water. The intensity of these bands decreases with temperature what demonstrate the desorption of the water during the heating of the samples. FTIR spectrum of the Tex (**Figure 3b**) shows the set of the absorption peaks in the region of 1200-1700 cm^{-1}, which are attributed to the stretching mode of aromatic CN heterocycles. The presence of C-H out-of-plane bonds in aromatic domains are proved by peak at 890 cm^{-1} and a sharp peak with the maximum at 808 cm^{-1} belongs to the breathing mode of s-triazine units. Peaks in the region above 3000 cm^{-1} evidenced the stretching vibrations of N-H bonds. FTIR spectra of the 1:1 composites (**Figure 3c**) and represents the superposition of the spectra of both components TiO_2 and Tex.

The photodegradation activity (PA) of the studied samples are compared in **Figure 4**.
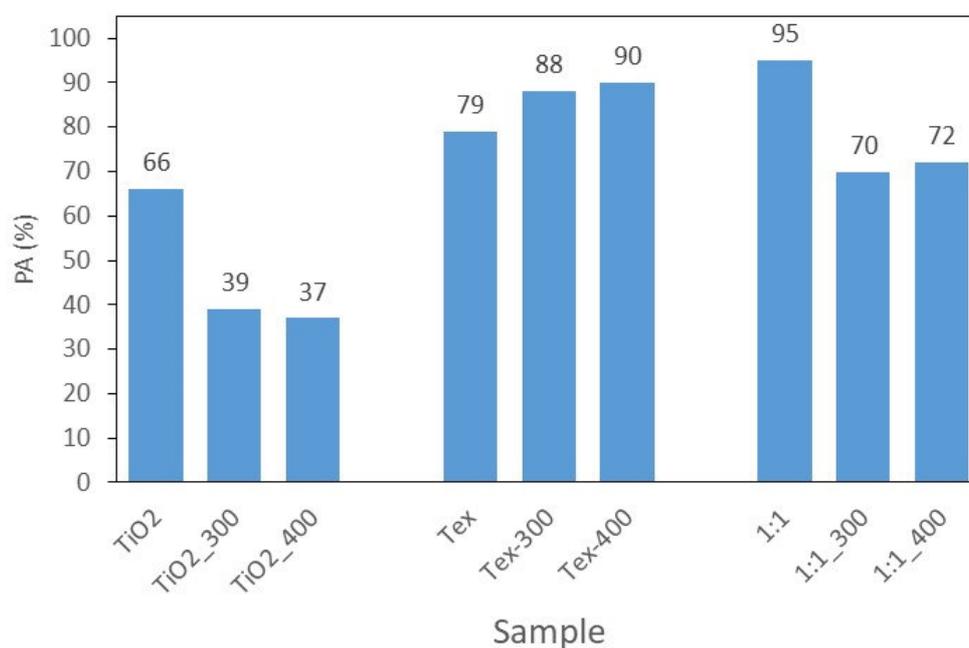
Figure 4 Comparison of the photodegradation activity of the prepared samples

For the TiO_2 series, the PA decreased with the temperature of the thermal treatment as evident in **Figure 4** what could be attributed to the growing of the anatase crystallite size. The PA for Tex increased with the temperature what could be related to the additional exfoliation of g-C_3N_4 particles. Comparing the PA values in the **Figure 4** the non-calcined 1:1 composite showed the best photocatalytical performance against AO7 and thermal treatment of this composite caused the decrease of PA.

3. CONCLUSION

The composite TiO_2/g-C_3N_4 (exfoliated) was prepared by mechanical mixing of both components in weight ratio 1:1. The composites were thermally treated at 300 and 400 °C. Characterization of the samples using XRD method as well as the IR spectroscopy revealed there was not any significant effect of the calcination temperature on the structure and character of the prepared composites. The observation of the particles of non-thermally treated composite using SEM showed strong agglomeration of g-C_3N_4 nanoflakes and homogenously distributed particles of TiO_2 over these agglomerates. The photodegradation activity of the TiO_2 and the composites TiO_2/g-C_3N_4 (exfoliated) decreases with the calcination temperature contrary to the exfoliated g-C_3N_4 for which the photodegradation activity increases. The highest photodegradation activity was observed for non-calcined composite TiO_2/g-C_3N_4 (exfoliated) and this composite was indicated as the most promising candidate for the photocatalytic applications. The further study will be focused on the evaluation of the stability of this composite and explanation of the photodegradation mechanism.

ACKNOWLEDGEMENTS

REFERENCES

[1] ZHENG, Y., ZHANG, Z., LI, C. A comparison of graphitic carbon nitrides synthesized from different precursors through pyrolysis. *Journal of Photochemistry and Photobiology A: Chemistry*. 2017. vol. 332, pp. 32-44.

[2] ZELINKA, J., HALFAROVÁ, P., VYKYDAL, D., LIŠKA, V., PRAUS, P., MATĚJKA, V. Design of experiment method for optimization of synthesis of G-C3N4 photocatalyst, In *NANOCON 2018 - Conference Proceedings, 10th Anniversary International Conference on Nanomaterials - Research and Application.* Ostrava: TANGER, 2019; pp 131-136.

[3] LI, Y., WANG, M.-Q., BAO, S.-J., LU, S., XU, M., LONG, D., PU, S. Tuning and thermal exfoliation graphene-like carbon nitride nanosheets for superior photocatalytic activity. *Ceramics International*. 2016. vol. 42, no. 16, pp. 18521-18528.

[4] ŠTENGL, V., HENYCH, J., SLUŠNÁ, M., ECORCHARD, P. Ultrasound exfoliation of inorganic analogues of graphene. *Nanoscale Research Letters*. 2014. vol. 9, no. 1, pp. 167-181.

[5] XU, J., ZHANG, L., SHI, R., ZHU, Y. Chemical exfoliation of graphitic carbon nitride for efficient heterogeneous photocatalysis. *Journal of Materials Chemistry A*. 2013. vol. 1 no. 46, pp. 14766-14772.

[6] JIANG, L., YUAN, X., PAN, Y., LIANG, J., ZENG, G., WU, Z., WANG, H. Doping of graphitic carbon nitride for photocatalysis: A reveiw. *Applied Catalysis B: Environmental*. 2017. vol. 217, pp. 388-406.

[7] MATĚJKA, V., ŠIHOR, M., RELI, M., MARTAUS, A., KOČÍ, K., KORMUNDA, M., PRAUS, P. Composites g-C3N4 and BiOIO3 for photocatalytic decomposition of N2O. *Materials Science in Semiconductor Processing*. 2019. vol. 100, pp. 113-122.

[8] LI, Y.-N., CHEN Z.-Y., WANG M.-Q., ZHANG L.-z., BAO, S.-J. Interface engineered construction of porous g-C3N4/TiO2 heterostructure for enhanced photocatalysis of organic pollutants, *Applied Surface Science*, 2018. vol. 440, pp. 229-236.

[9] SVOBODA, L., ŠKUTA, R., MATĚJKA, V., DVORSKÝ, R., MATÝSEK, D., HENYCH, J., MANČÍK, P., PRAUS, P. Graphene oxide and graphitic carbon nitride nanocomposites assembled by electrostatic attraction forces: Synthesis and characterization. *Materials Chemistry and Physics*. 2019. vol. 228, pp. 228-236.