DESIGN OF EXPERIMENT METHOD FOR OPTIMIZATION OF SYNTHESIS OF g-C_3N_4 PHOTOCATALYST

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Abstract

G-C_3N_4 is an intensively studied material for photocatalytic applications, mainly for the degradation of pollutants in water and air. The thermal polymerization of suitable precursors (urea, melamine, dicyanamide etc.) is the most often used approach for the g-C_3N_4 synthesis. In this research, g-C_3N_4 was prepared by the thermal polymerization of melamine and calcination conditions were tuned using Design of Experiment approach (DOE). Five factors, such as the temperature ramp rate, final temperature, holding time, cooling rate and amount of initial melamine, were preselected and tested on two levels: 3 and 10 °C/min, 500 and 550°C, 0 and 1h, shock and slow cooling, 2.5 and 10 g. A half testing plan including 16 calcination experiments was set using fractional factorial design. The yield of final products of calcination was used as the measured output of the experiments. The photogeradation activity against the model dye acid orange 7 (AO7) was evaluated for selected samples. The results indicated the weight loss of melamine for a given temperature depended mainly on its initial weight and heating rate. The photodegradation activity was higher for the samples calcined at the temperature of 500 °C.

Keywords: Graphitic carbon nitride, melamine, polymerization, DOE, photocatalysis

1. INTRODUCTION

The photocatalysts are materials studied for their potential to degrade organic, but also inorganic compounds and this feature can be utilized, for example, for cleaning of the air and water [1]. The principle of functionality of these materials is the light assisted generation of electron - hole pairs. The energy of incident light has to be equal or lower that the band gap energy of a photocatalyst. For example, widely studied TiO_2 and ZnO are being intensively studied as the efficient photocatalysts [2,3]. The band gap energy of both TiO_2 and ZnO reachs the values close to 3.2 eV what means their photoactivity can be evoked by the light with wavelength equal or lower to 386 nm (UVA region). Practically, it means that less than 10 % of the sun light can be used for activation of these materials and thus the artificial UV light has to be used for the efficient photocatalytic process over these materials.

Although the many approaches for shifting the photoactivity of these materials to the VIS part of spectra already exist (mainly metal and non-metal doping). The efforts for searching of photocatalysts active in the visible range of spectra led, for example, to indication of g-C_3N_4 as the promising material for this purpose [4]. The band gap energy of g-C_3N_4 reaches the value 2.5 eV what means that it can be activated with light of the wavelength equal or lower than 495 nm. The preparation of g-C_3N_4 is based on the thermal treatment of suitable precursors, for example, melamine [5]. During heating the precursors of g-C_3N_4 melam, melem and melon as the by-products of the melamine thermal polymerization were found [6]. Interestingly, there is the number of papers dealing with the calcination of melamine with the aim to prepare g-C_3N_4 with high photoactivity. The reported calcination temperature ranges from low temperatures below 500°C to high temperatures above 600 °C [7,8]. Undoubtedly, there are other factors which could affect the final photoactivity

of synthesized g-C_3N_4 as well as the yield of final products, for example, the heating rate and holding time at a given temperature.

Due to the variety of factors, which are considered to have the effect on the melamine calcination, DOE represents a systematic approach for the creation of a testing plan and the statistical evaluation of relations between factors affecting a studied process and the outputs of experiments [9]. DOE is a systematic method to determine the relationship between factors affecting a process and the output of that process. In other words, DOE allows to find factors that have an influence on the production process and determine their optimal values of the factors. When experimenting, we tried to find the relationship "cause-effect" when we used the targeted input changes to achieve changes in output. We tried to capture and describe this relationship using mathematical methods. From these outputs, it is possible to analyse many links and patterns about the process.

Typical the DOE methodology is based on several steps. The first step is the analysis of studied process and indication of relevant factors influencing the studied process, setting their levels and defining the output(-s) of the process. The number of factors and the number of levels give the total number of experiments which need to be performed according to the equation (1).

$$n = 2^k \tag{1}$$

where n is the number of experiments, k is the number of factors and 2 is the number of levels.

The further steps of DOE include i) preparation of a testing plan, iii) performing of tests, collection of outputs and iv) evaluation of the outputs. Based on the number of the factors and levels, the number of experiments, which are necessary to be performed, could be high and thus the methods of reduced testing plan are also adopted. Half testing plans based on the fractional factorial design [10] or the Taguchi approach [11] are the typical examples.

In our research we focused on the evaluation of applicability of the half testing plan for tuning the calcination of melamine with the aim to identify the best combination of selected factors with respect to the yield of final products. The defined five factors, such as temperature, heating rate, hold time, cooling rate and the amount of melamine, were tested at two levels (minimum, maximum) resulted in 16 calcination experiments. The yield of the calcination product was used as the main output of the DOE experiments. The photodegradation of AO7 was measured for the prepared materials.

2. EXPERIMENTAL

2.1. Design of experiment

The half testing plan and its individual experiments were planned using the statistical software Minitab 17. Five factors, which should have the major influence on the calcination of melamine, were identified and are summarized in **Table 1**.

Table 1 Selected factors and defined levels

Factor	Identification	Level	
		Low	High
A	Temperature (°C)	500	550
B	Heating rate (°C·min^{-1})	3	15
C	Hold time (h)	0	1
D	Cooling rate	F	S
E	Weight of melamine (g)	2.5	10

Note: The cooling rate levels were fast (F) and slow (S).

Using the equation (1) the number of the experiments for full factorial testing plan for the combination of the factors and levels listed in **Table 1** is equal to 32. The half testing plan included 16 experiments selected by Minitab 17 and is shown in **Table 2**. Variable "-1" represents the low factor level and "+1" is the high factor level.

Table 2 The definition of the half testing plan, the average yield of the final product

No.	Factors (Inputs)					Output
	A	B	C	D	E	Yield (%)
1	-1	-1	-1	-1	1	64
2	1	-1	-1	-1	-1	53
3	-1	1	-1	-1	-1	47
4	1	1	-1	-1	1	50
5	-1	-1	1	-1	-1	57
6	1	-1	1	-1	1	57
7	-1	1	1	-1	1	49
8	1	1	1	-1	-1	42
9	-1	-1	-1	1	-1	60
10	1	-1	-1	1	1	63
11	-1	1	-1	1	1	55
12	1	1	-1	1	-1	47
13	-1	-1	1	1	1	64
14	1	-1	1	1	-1	54
15	-1	1	1	1	-1	47
16	1	1	1	1	1	47

2.2. Calcination experiments and photodegradation activity measurement

Melamine (Karl Roth GmbH, Germany) was used for all calcination experiments. The calcination was performed in a muffle furnace (LAC, Czech Republic). Glazed ceramic crucibles with glazed ceramic covers were for the calcination experiments. The calcination was performed in static air atmosphere. Two replicas for each experiment defined in **Table 2** were performed. TiO_2 P25 (Degussa) was used for the comparison of the photodegradation activity of the prepared samples.

The photodegradation activity of the prepared samples was tested by the photocatalytic decomposition of AO7 (Synthesia,a.s., Czech Republic). In the typical experiment, the tested samples were weighted (0.0500 g) into a glass bowl filled with 150 ml of distilled water mixed using an electromagnetic stirrer (300 rpm). After 5 min of stirring 15 ml of the AO7 solution ($c = 7.136 \cdot 10^{-4}$ mol·dm^{-3}) was added. The resulting suspension was further stirred in dark for 1 h to achieve adsorption equilibrium. After this period, 5 ml of the suspension was taken and filtered under vacuum using a membrane filter with porosity of 0.4 μm (Pragopor, Czech Republic). The absorbance of filtered solutions was measured at 480 nm using a HELIOS Σ spectrometer (ThermoSpectronic, USA) and as A_0. In the same time a source of UV light (BLB 36 W, NARVA) was turned on and the sample was subjected to irradiation for 120 min. After this step, 10 ml of sample was taken out of the stirred suspension and filtered using a membrane filter. The absorbance of the filtered solution was measured at 480 nm and assigned A_{120}.

UV-VIS diffuse reflectance spectroscopy measurements (UV-VIS DRS) were performed using Shimadzu UV-2600 spectrometer (Shimadzu, Japan) equipped with integrating sphere IRS-2600Plus (Shimadzu, Japan).

The samples were pressed inside the holder and DRS spectra were acquired in range 300 - 500 nm. BaSO4 powder (Nacalai Tesque, Inc., extra pure reagent grade) was used for the setting of the baseline. The Tauc's plots were used for the evaluation of indirect band gap values.

3. RESULTS AND DISCUSSION

The calcination yields obtained during the experiments defined by the half testing plan are shown in **Table 2**. The effect of the factor levels on the yields of the final product is expressed in **Figure 1**. Based on **Figure 1** the positive effect of the low temperature (500 °C), low heating rate (3 °C·min^{-1}) and low duration of the calcination on the yield was observed. However, an opposite effect of the level of cooling rate and weight of the sample was observed. Practically, **Figure 2** shows us that for the maximum yield we should perform the calcination with the low heating rate, at the lower temperature, with the low holding time but the cooling rate should be faster and the higher amount of melamine should be used.

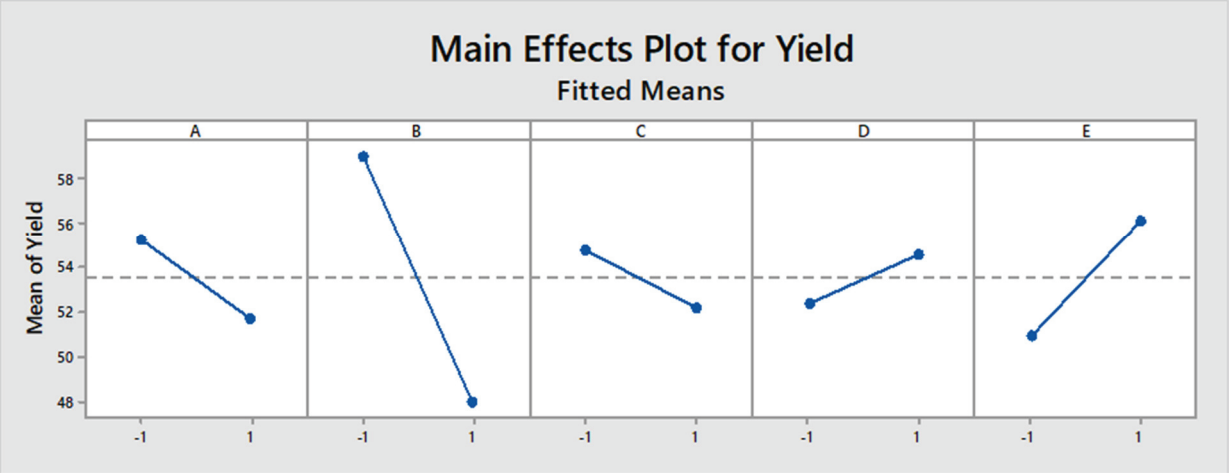

Figure 2 The effect of the level of given factor on the process of melamine calcination

The experiments ranking based on the yields is shown in **Figure 2**. **Figure 2** indicated the sample 8 as the sample with the lowest yield, whereas the samples 1 and 13 as that with the highest product yield.

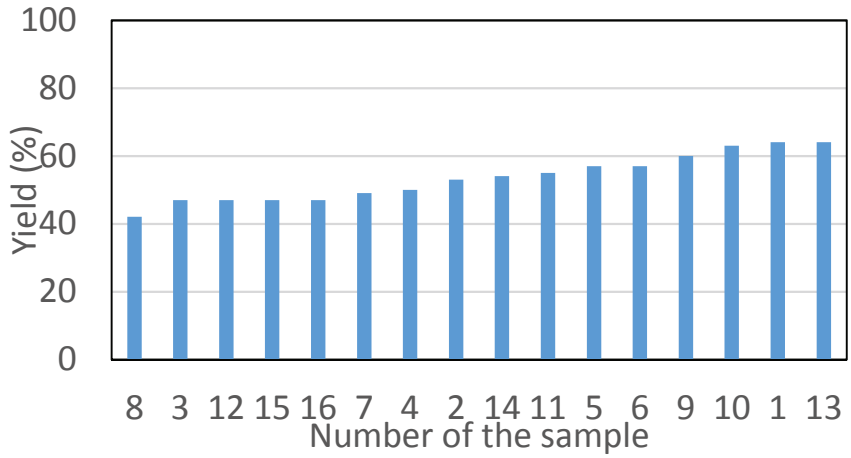

Figure 2 The ranking of the samples based on the yield of the melamine calcination

For the samples 1, 8 and 13 the photodegradation activity against AO7 was measured. After 2 h of the UVA irradiation the sample 8 showed 43 % of the AO7 degradation, whereas the sample 1 showed 80 % and sample 13 showed 87 % of the AO7 degradation. The reference sample TiO_2 P25, which is usually used as

the reference material for evaluation of the photodegradation efficiency, showed 71 % of the AO7 degradation after the same time.

The morphology of the sample 13 was studied using SEM technique and the image is shown in **Figure 3a**). The stacked particles of the platy character formed the irregularly shaped agglomerates. The UV-VIS DRS spectra of the samples 1, 8 and 13 are shown in **Figure 3b**). The band gap energies of the samples 1 and 13 are similar and reached the values 2.81 and 2.79 eV, respectively; the calculated band gap energy of sample 8 reached value 2.73 eV.

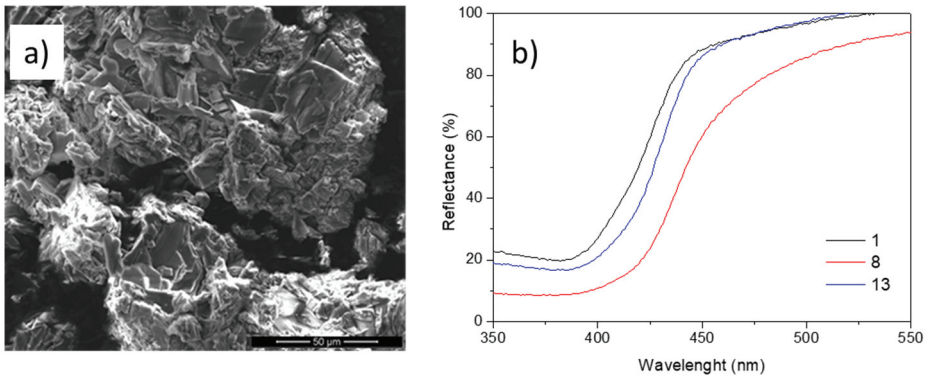

Figure 3 SEM image of the sample 13 (a), reflectance spectra of the samples 1, 8 and 13 (b)

4. CONCLUSION

The half testing plan approach as one of the DOE methods was used for the optimization of the melamine calcination with respect to the yield of the final product. The results indicated the optimal calcination conditions were: i) the calcination temperature of 500 °C, ii) the heating rate of 3 °C·min^{-1} and iii) the weight of melamine 10 g as the optimal conditions with respect to the yield of the calcination. The measured photoactivity indicated the samples 1 and 13 as more efficient in comparison to the sample 8. The photodegradation activity of the samples 1 and 13 was higher than the reference sample TiO_2 P25.

The next step of our research will be the finalization of the photodegradation activity according to the half testing plan and using the DOE approach for the indication of the factor(-s) of the melamine calcination with significant effects on the photodegradation activity of final products. In parallel the full testing plan including next 16 calcination experiments will be performed and the same outputs (yield and photodegradation activity) will be measured. The results of the full testing plan will be compared with the results of the half testing plan. The selected samples will be characterized using the methods of chemical and phase analysis. The relations between observed characteristics of the final samples, yield and photodegradation activity will be described.

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REFERENCES

[1] REDDY, P.A.K., REDDY, P.V.L., KWON, E., KIM, K.H, AKTER, T. and KALAGARA, S. Recent advances in photocatalytic treatment of pollutants in aqueous media. *Environment International*. 2016, vol. 91, pp. 94-103.

[2] LEE, S.-Y. and PARK S.-J. TiO2 photocatalyst for water treatment applications. *Journal of Industrial and Engineering Chemistry*. 2013, vol. 19, no. 6, pp. 1761-1769.

[3] DI MAURO, A., FRAGALA, M.E., PRIVITERA, V. and IMPELIZZERI, G. ZnO for application in photocatalysis: From thin films to nanostructures. *Materials Science in Semiconductor Processing*. 2017, vol. 69, pp. 44-51.

[4] MAMBA, G. and MISHRA, A.K. Graphitic carbon nitride (g-C3N4) nanocomposites: A new and exciting generation of visible light driven photocatalysts for environmental pollution remediation. *Applied Catalysis B: Environmental*. 2016, vol. 198, pp. 347-377.

[5] DEVTHADE, V., KULHARI, D. and UMARE, S.S. Role of precursors on photocatalytic behavior of graphitic carbon nitride. *Materials Today: Proceedings*. 2018, vol. 5, no. 3, pp. 9203-9210.

[6] KESSLER, F.K., ZHENG, Y., SCHWARZ, D., MERSCHJANN, C., SCHNICK, W., WANG, X. and BOJDYS, M.J. Functional carbon nitride materials - design strategies for electrochemical devices. *Nature Reviews Materials*. 2017, vol. 2, no. 6, pp. 1 - 17.

[7] ZENG, Y., LIU, X., LIU, C., WANG, L., XIA, Y., ZHANG, S., LUO, S., PEI, Y. Scalable one-step production of porous oxygen-doped g-C3N4 nanorods with effective electron separation for excellent visible-light photocatalytic activity. *Applied Catalysis B: Environmental*. 2018, vol. 224, pp. 1-9.

[8] KOČÍ, K., RELI, M., TROPPOVÁ, I., ŠIHOR, M., KUPKOVÁ, J., KUSTROWSKI, P. and PRAUS P. Photocatalytic decomposition of N2O over TiO2/g-C3N4 photocatalysts heterojunction. *Applied Surface Science*. 2017, vol. 396, pp. 1685-1695.

[9] JIJU A. *Design of Experiments for Engineers and Scientists*. 1st ed. Elsevier, 2003. pp. 109.

[10] MONTGOMERY, D.C. *Design and analysis of experiments*. 6th ed. Hoboken, NJ: John Wiley, 2005. pp 752.

[11] ROY, R.K. *Design of experiments using the Taguchi approach: 16 steps to product and process improvement*. New York: Wiley, 2001. pp 560.