# PHOTOCATALYTIC REACTIVATION OF g-C$_3$N$_4$ BASED NANOSORBENT

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## Abstract

In this work, we present new preparation method, photocatalytic activity and photocatalytic reactivation of photoactive layered graphitic carbon nitride (g-C$_3$N$_4$), which was incorporated into silica structure containing zinc-silicate nanoparticles (ZnO-$m$·SiO$_2$). Prepared material exhibits more than ten times larger specific surface area than pure bulk g-C$_3$N$_4$. Material was prepared by sonication of intensively stirred aqueous solution of zinc acetate and g-C$_3$N$_4$ while sodium water glass was slowly added by drops into the mixture. Sodium water glass reacted with zinc acetate, which was in excess, and composite ZnO-$m$·SiO$_2$ nanoparticles has precipitated on g-C$_3$N$_4$ nanosheets. Prepared nanodispersion was turned into powder material by vacuum freeze drying technique. This technique preserves most of particles specific surface area by conserving chaotic arrangement of given particles in water solution. Prepared powder was further calcinated at 500 °C for one hour. Photocatalytic reactivation was tested on TiO$_2$ and ZnO-$m$·SiO$_2$/g-C$_3$N$_4$ nanocomposite. Material was stirred in the dark with aqueous solution of methylene blue for one hour to reach an adsorption-desorption equilibrium. Material with adsorbed dye on its surface was than separated and collected from solution by centrifugation, transferred into pure demineralised water and adsorbed dye was than decomposed under LED light irradiation within half an hour. Dispersion was centrifugated again to separate by-products, dried by vacuum freeze drying and subjected to sorption process again. Although kinetic characteristics for both materials were different, sorption properties of both materials did not change after reactivation.

**Keywords:** Photocatalysis, nanoparticles, graphitic carbon nitride

## 1.    INTRODUCTION

One of the major threats we have to face nowadays is an environmental pollution, which is getting worse with everyday industrial activity and automotive transport. After discovery of photocatalytic reaction and its possible use in degradation of harmful substances, many researchers are trying to prepare photocatalytic materials, which could be used in removal of these pollutants. We can remove for example organic compounds from water [1, 2] or inorganic substances (such as CO, CO$_2$ or oxides of nitrogen NO$_x$ and sulphur) from air [3, 4]. Due to the extent of pollution, it is necessary to prepare photocatalytic materials with cheap and effective production technology. Nanoparticles and other nanomaterials are getting higher attention because of the nature of photocatalysis. It is process which takes place on the surface of catalyst and therefore increasing the specific surface area (SSA) can lead to increase in photocatalytic activity. Nanomaterials can provide desired surface areas and maximize the photocatalytic reaction efficiency. The most feasible bottom-up method for preparation of nanomaterials is controlled precipitation reaction in liquid medium. We usually need a dry form, due to better handling and wider applicability. Drying wet particles in the furnace can lead to final dry powder with lower SSA value due to particle agglomeration during drying. Vacuum freeze drying turns out to be a promising method for preserving high specific surface area of nanomaterials. Among the well-known photocatalysts belong ZnO [5], ZnS [6] or TiO$_2$ [7]. TiO$_2$ is the most popular photocatalitic material used in many studies as standard because of its good photocatalytic activity. Practical applications of photocatalytic

processes do not stop with degradation of unwanted substances in environment. Photocatalysts can be also further used for hydrogen production [8] or photocatalytic synthesis [8].

Considering the Sun as the best source of green, inexhaustible energy, many researchers are trying to find photocatalyst utilizing as much as possible from solar spectrum. Problem with wide-gap semiconductors is that they need to be excited by UV-irradiation, which is mostly filtered by ozone in atmosphere and represents minority of irradiation getting to the Earth's surface. Therefore, photocatalysts which would be active in visible light range are getting great attention. One of the possible candidates is layered graphitized carbon nitride (g-$C_3N_4$). It is polymeric non-metal semiconductor with excellent thermal and chemical stability. Its band gap is about 2.7 eV wide [9]. Graphitized $C_3N_4$ was successfully used as an efficient visible light active photocatalyst for degradation of organic pollutants, organic synthesis, water splitting or reduction of $CO_2$ [8].

Another way how to remove pollutants from the water or the air are sorption processes. By this way, the harmful substances are caught at surface of suitable sorbent and removed from the environment. One of the greatest problems of sorbents is saturation. The sorption surface reaches its maximum capacity and cannot catch another molecules of pollutant. Sorbent has to be replaced or reactivated.

In this work, we successfully incorporated layered g-$C_3N_4$ into ZnO-$m \cdot SiO_2$ nanoparticles and performed photocatalytic reactivation. This composite has specific surface area more than ten times higher than bulk g-$C_3N_4$, even higher than pure exfoliated g-C3N4 nanosheets [10] and exhibits photocatalytic activity in visible light spectra. Synthetized photocatalyst was characterized by EDX, BET analysis, TEM and subjected to test of sorption and photocatalytic activity.

## 2. EXPERIMENTAL

### 2.1. Materials and chemicals

Chemical used for experiments are zinc acetate of 99 % purity purchased from PENTA s.r.o., sodium water glass 38-40 °Bé ($Na_2SiO_3$) with modulus of 3 purchased from company Vodní sklo, a.s., $TiO_2$ (Evonik Degussa P25) and melamine of 99% purity purchased from Sigma-Aldrich spol. s.r.o. For all aqueous solutions, deionized water was used.

### 2.2. Preparation of g-$C_3N_4$

Bulk g-$C_3N_4$ was prepared by heating melamine in laboratory furnace to 550 °C in air for 4 hours. Temperature was raised from ambient temperature to desired one with step of 2 °C per minute. Material was than comminuted by grinding in agate mortar and further exfoliated by heating up to temperature of 500 °C with step of 2 °C per minute [10].

### 2.3. Precipitation of ZnO-$m \cdot SiO_2$ nanoparticles on g-$C_3N_4$ sheets

1 g of zinc acetate and 0.4 g of g-$C_3N_4$ was mixed in 300 ml of deionised water, sonicated in ultrasonic reactor with power of 50 W/L and intensively stirred (1500 RPM) for 1 hour. Sodium water glass was diluted in deionised water in ratio of 1:340 to get low concentrated water glass. During this one hour of g-$C_3N_4$ nanodispersion sonication in the zinc acetate solution, 200 ml of low concentrated water glass was added to the solution by peristaltic pump ended with a needle to ensure dripping drop by drop. Dispersion was than four times centrifuged at 9000 RPM for 10 minutes to separate material from redundant water solution of precursors.

To get a dry powder, the material was sonicated in deionised water, subsequently rapidly frozen to suppress aggregation of nanoparticles during segregation and placed in vacuum recipient of lyophilizer for vacuum freeze drying. Under the defined pressure and surface temperature, the frozen water molecules are sublimed

and nanostructure with high specific surface area is created. Pressure and temperature in recipient determine rate of sublimation and therefore structure of resulting material.

### 2.4. EDAX and TEM analysis

EDX analysis on scanning electron microscope SEM FEI Quanta 650 FEG was used to determine the composition of final nanocomposite powder material.

A transmission electron microscope Jeol JEM 1230 with accelerating voltage of 80 kV was used to take TEM micrograph of the nanostructure.

### 2.5. Specific surface area

Specific surface area was measured by dynamic BET analysis on Qsurf HORIBA SA9601 which works in continuous regime. Dry form of a sample was degassed for 5 hours at 150 °C and then subjected to multipoint analysis (six-point analysis was chosen for all samples).

### 2.6. Continual measuring of adsorption of simulant dye

For determination of adsorbed amount of dye, we used reactor based on measuring light intensity in a real-time mode. The reactor consists of vessel, where the dispersion of sorbent powder material and organic dye is intensively stirred. The vessel temperature is kept up to 20°C by thermostat system. The decrease of the dye concentration (adsorbed amount) is determined by measuring of diffused and backscattered light from a laser. The laser is located on the top cover of the vessel and light goes to the nonlinear surface of the dispersion in the vessel. There it diffuses in the dispersion and backscatters to the detector (Ocean Optics USB4000-UV-VIS, Spectrum Suite software), which is also on the cover of the vessel next to the laser light source. The measured intensity depends on dye concentration and with proper reference measurement we are able to calculate the dye actual remaining concentration, which is a significant advantage against other measurement techniques, where samples with not negligible volume need to be extracted first from the solution and then particles have to be removed by centrifugation.

### 2.7. Photocatalytic reactivation

Sorption process was performed in the chamber as described in 2.6. Photocatalytic sorbent was stirred in the dark with aqueous solution of the dye for one hour to reach an adsorption-desorption equilibrium. Photocatalytic sorbent with adsorbed dye on its surface was than separated and collected from solution by centrifugation at 9000 RPM for 10 minutes and transferred into pure demineralised water with volume of 50 ml. Photocatalytic reaction was activated by narrow LED light source on the top of the vessel. Adsorbed dye was decomposed under 415 nm LED irradiation within half an hour. Dispersion was centrifugated again to separate products of photocatalysis, dried by vacuum freeze drying and subjected to sorption process again.

We used dispersion of 0.05 g of photocatalytic sorption material dispersed in 50 ml of demineralized water. As a dye simulant, we used methylene blue. Starting concentration of the dye was 2 mg/l. The maximum emission of LED light source for activation of photocatalytic reaction was at 415 nm. Measuring laser light source peak was at 637 nm and intensity measurement was done as an intensity integral from 634 to 640 nm. $TiO_2$ P25 was used as standard for comparison, where UVA LED light source was used for decomposition of adsorbed methylene blue before repeated sorption test.

## 3. RESULTS AND DISCUSSION

Nanocomposite ZnO-$m$·$SiO_2$/g-$C_3N_4$ was prepared by sonication of intensively stirred mixture of precursors and dried by vacuum freeze drying (see chapter 2.3 for more details). Dried form was calcinated for 1 hour at 500 °C.

The specific surface area has important impact on sorption material performance. The SSA of ZnO-$m$·SiO$_2$/g-C$_3$N$_4$ was determined as 238 m$^2$/g. It has higher SSA than exfoliated g-C$_3$N$_4$, which has SSA of 157 m$^2$/g. It is mostly due to silica structure. SSA of TiO$_2$ and bulk g-C$_3$N$_4$ was 68 m$^2$/g and 23 m$^2$/g, respectively. TEM micrograph shows coverage of exfoliated g-C$_3$N$_4$ nanosheets by ZnO-$m$·SiO$_2$ nanoparticles (**Figure 1**).
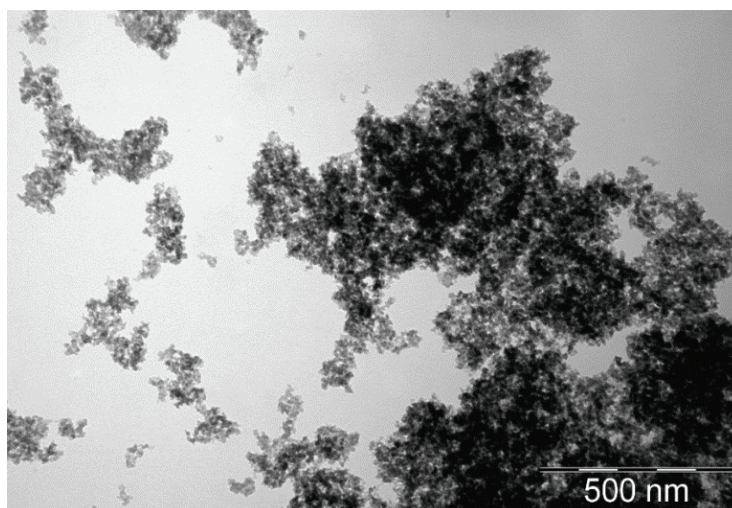


**Figure 1** TEM micrograph of ZnO-$m$·SiO$_2$/g-C$_3$N$_4$ nanocomposite

EDX analysis from SEM microscope showed its composition (**Figure 2**) and confirmed ZnO-$m$·SiO$_2$ structure connected with g-C$_3$N$_4$ nanosheets.
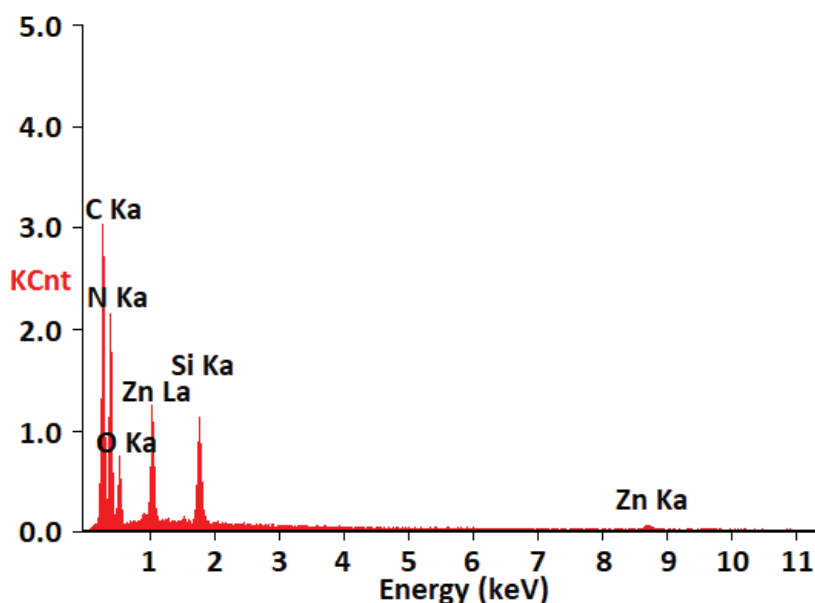


**Figure 2** EDX element analysis of ZnO-$m$·SiO$_2$/g-C$_3$N$_4$ nanocomposite powder

Exfoliated g-C$_3$N$_4$ nanosheets and prepared composite were subjected to the test of photocatalytic activity. It took 50 minutes to decompose adsorbed methylene blue in the presence of pure exfoliated g-C$_3$N$_4$ and 75 minutes for ZnO-$m$·SiO$_2$/g-C$_3$N$_4$. Nanocomposite ZnO-$m$·SiO$_2$/g-C$_3$N$_4$ was more suitable for sorption processes due to its higher specific surface area and possibility of further modifications allowed by silica structure [11].

On **Figure 3** are kinetic characteristics of methylene blue sorption on $TiO_2$ and on **Figure 4** kinetic characteristics of methylene blue sorption on ZnO-$m$·$SiO_2$/g-$C_3N_4$.
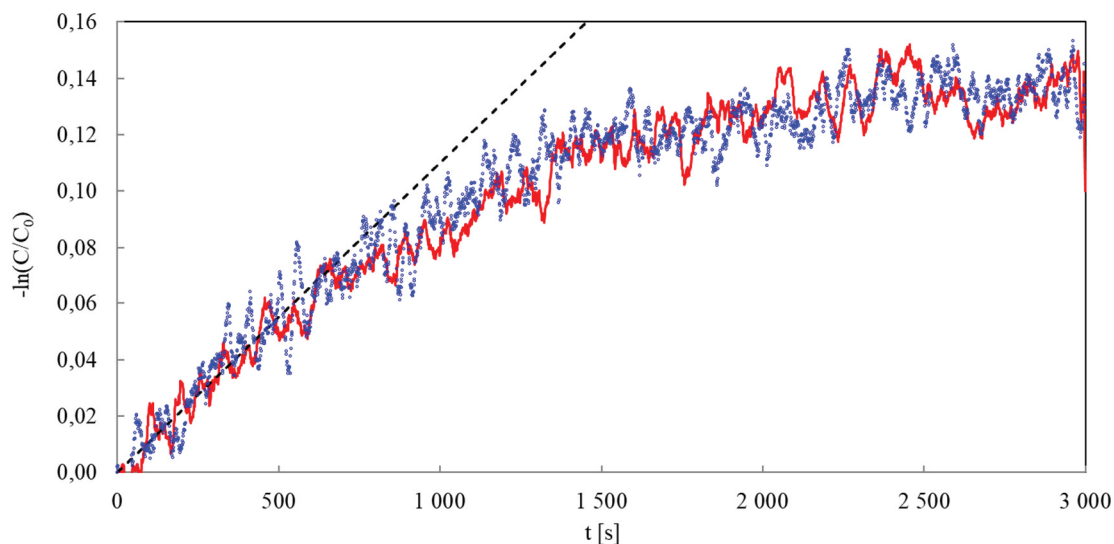


**Figure 3** Kinetic characteristics of methylene blue sorption on primary pure $TiO_2$ (blue) and sorption of the same material in secondary form after photocatalytic reactivation (red). Dashed line is linear regression in linear area used for calculation of rate constant

The sorption capacity of $TiO_2$ remained almost same after photocatalytic reactivation. $TiO_2$ is not good sorbent especially because of its SSA but it was used as comparison because of its standard photocatalytic properties.
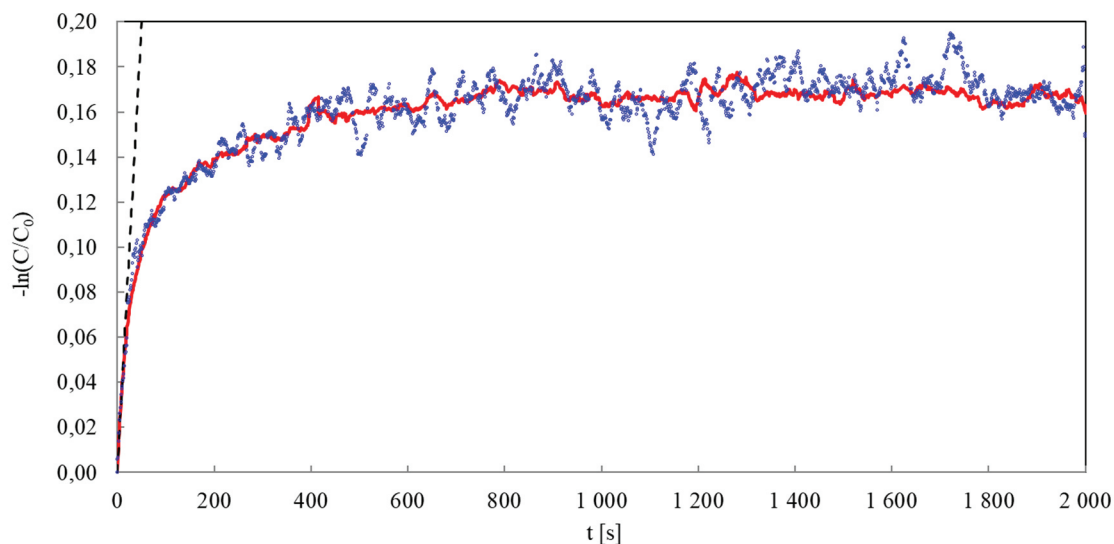


**Figure 4** Kinetic characteristics of methylene blue sorption on primary pure ZnO-$m$·$SiO_2$/g-$C_3N_4$ (blue) and sorption of the same material in secondary form after photocatalytic reactivation (red). Dashed line is linear regression in linear area used for calculation of rate constant.

Nanocomposite ZnO-$m$·$SiO_2$/g-$C_3N_4$ showed much better performance than $TiO_2$. The half-time of sorption on ZnO-$m$·$SiO_2$/g-$C_3N_4$ nanocomposite was only 30 s. Rate constants of adsorption tests were calculated from linear parts of acquired data for both samples. Values are 0,004 $s^{-1}$ for ZnO-$m$·$SiO_2$/g-$C_3N_4$ nanocomposite and 0.0001 $s^{-1}$ for $TiO_2$. It showed that ZnO-$m$·$SiO_2$/g-$C_3N_4$ is much more suitable for sorption processes.

## 4.  CONCLUSION

Nanocomposite ZnO-$m \cdot$SiO$_2$/g-C$_3$N$_4$ was successfully prepared by sonication of intensively stirred dispersion of exfoliated g-C$_3$N$_4$ and zinc acetate while sodium water glass was slowly dripping into the solution. Photocatalytic sorbent was characterized by TEM and EDX and was subjected to sorption tests. The presence of silica structure containing composite ZnO-$m \cdot$SiO$_2$ nanoparticles on g-C$_3$N$_4$ nanosheets was confirmed. SSA of ZnO-$m \cdot$SiO$_2$/g-C$_3$N$_4$ nanocomposite, determined by BET analysis, is 238 m$^2$/g. Complete degradation of methylene blue in 75 minutes confirmed its photocatalytic activity and reactivation after saturation with methylene blue of given material was performed.

Nanocomposite ZnO-$m \cdot$SiO$_2$/g-C$_3$N$_4$ and TiO$_2$ were subjected to photocatalytic reactivation under the LED light source irradiation. Results confirmed that this method can be used for full reactivation of photocatalytic sorbents. Nanocomposite ZnO-$m \cdot$SiO$_2$/g-C$_3$N$_4$ showed more faster sorption than TiO$_2$. The half-time of sorption process was only 30 s. In the follow up research the influence of ZnO-$m \cdot$SiO$_2$ porosity and its ratio with g-C$_3$N$_4$ on reactivation process will be studied and optimized. Although there was difference in sorption properties of both samples, photocatalytic reactivation was successful, reproducible and sorption capacity remained the same for both samples after photocatalytic reactivation. It indicates universality of this method and its independency on sorption kinetics.

## ACKNOWLEDGEMENTS

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