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### Photocatalytic H<sub>2</sub> production from aqueous solutions of hydrazine and its derivatives in the presence of nitric-acid-activated graphitic carbon nitride

Alexandra E. Raevskaya<sup>a</sup>, Yaroslav V. Panasiuk<sup>a</sup>, Ganna V. Korzhak<sup>a</sup>, Oleksandr L. Stroyuk<sup>a,\*</sup>, Stepan Ya. Kuchmiy<sup>a</sup>, Volodymyr M. Dzhagan<sup>b,c</sup>, Dietrich R.T. Zahn<sup>b</sup>

<sup>a</sup> L. Pysarzhevsky Institute of Physical Chemistry of National Academy of Sciences of Ukraine, Kyiv 03028, Ukraine

<sup>b</sup> Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany

<sup>c</sup> V. E. Lashkaryov Institute of Semiconductors Physics, National Academy of Sciences of Ukraine, Kyiv 03028, Ukraine

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#### ABSTRACT

A treatment of graphitic carbon nitride (GCN) with concentrated nitric acid imparts GCN with the photocatalytic activity in hydrogen evolution from aqueous solutions of hydrazine hydrate, unsymmetric dimethylhydrazine (DMH) and hydrazinium sulfate under illumination with the UV light and in the presence of a Pd/SiO<sub>2</sub> co-catalyst. The rate of photocatalytic water reduction was found to be maximal in the presence of 3–5 M DMH and 12–14 M hydrazine hydrate and comparable to the hydrogen evolution rate in similar systems based on TiO<sub>2</sub> Evonik P25.

The X-ray photoelectron spectroscopy of the activated GCN revealed that the acid treatment results in the elimination of some of the nitrogen atoms in the heptazine building blocks of the GCN and formation of carboxylic groups, the modification extent increasing with an increase of both duration of the acid treatment and the GCN synthesis temperature.

The activation effect observed after the acid treatment of the GCN is assumed to originate from the participation of the introduced defects in the trapping and interfacial transfer of the photogenerated charge carriers. The maximal photoactivity was observed for the activated GCN produced at 500 °C followed by a 2-h contact with the concentrated HNO<sub>3</sub>.

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#### 1. Introduction

Photocatalytic splitting of water to hydrogen and oxygen as well as water reduction with various sacrificial electron donors by using the inexhaustible solar energy is one of the challenges faced by the modern photochemistry and material science. A broad assortment of sacrificial compounds that can be used as a fuel to reduce water—from sustainable products of agriculture to waste by-products of various chemical industries [1–8]. A very attractive way of arranging the photocatalytic hydrogen production is in combining the water reduction process with the simultaneous

\* Corresponding author at: Laboratory of Organic Photovoltaics and Electrochemistry, L.V. Pysarzhevsky Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 31 Nauky av 03028, Kyiv, Ukraine.

*E-mail addresses:* alstroyuk@ukr.net, stroyuk@inphyschem-nas.kiev.ua (O.L. Stroyuk).

decomposition of toxic and persistent compounds, such as industrial wastes, disarmament wastes as well as warfare agents and chemical weapons used as sacrificial donors. Among such toxic compounds, a special place belongs to hydrazine and its derivatives, in particular to the unsymmetric 1,1-dimethylhydrazine (DMH) and hydrazinium sulfate (HS).

The unsymmetric DMH is a widespread component of rocket fuels broadly utilized in the aerospace program of the former Soviet Union. The disarmament program launched in the 1980–90ths left behind large stockpiles of DMH that need to be utilized, amounting after 1992 to around 5000 tons in Ukraine (the country of origin of some of the present authors) and more than 80,000 tons in Russia [9]. The DMH contacting with air oxygen either by a leakage to soil or during burning procedures can form very carcinogenic and persistent nitroso dimethylamine [9,10] and therefore other "green" approaches to the DMH utilization are needed.

A good alternative to the thermal oxidation can be the photocatalytic oxidation of hydrazine and its derivatives. It was shown

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that by using  $TiO_2/Pt$  heterostructures as photocatalysts the DMH can be readily degraded to  $CO_2$ , HNO<sub>3</sub>, water and N<sub>2</sub> avoiding the formation of the nitroso dimethylamine as a by-product [10]. At the same time, it was shown as early as in 1982 that hydrazine can be used as a sacrificial electron donor to photocatalytically reduce water to H<sub>2</sub> [11].

Another vital issue that should be addressed in the design of efficient photocatalytic systems for hydrogen production is the feasibility to carry out the photoprocess under visible light supplied by the solar illumination. The issue remains a challenge till the present day as the most active semiconductor photocatalysts either can absorb only the UV light (TiO<sub>2</sub>, ZnO), or are prone to the photocorrosion emitting toxic metals to environment (CdS), or have a low conduction band potential that is insufficient for water reduction to H<sub>2</sub> (WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) [2,3,6]. Recently, the graphitic carbon nitride (GCN) emerged as new visible-light-sensitive photocatalyst of water splitting and other important light-driven redox processes [12–16]. The GCN features an attractive combination of high stability and availability, a low toxicity, relatively strong absorption of the UV and visible light down to 460-470 nm, as well as the conduction and valence band potentials favorable for both water reduction and oxidation [12–14]. The GCN coupled to an appropriate cocatalyst can act as a photocatalyst of water reduction to molecular hydrogen with a variety of sacrificial donors, such as substituted amines, alcohols and inorganic sulfur-containing salts [14]. At the same time, the feasibility of using hydrazine and its derivatives as electrons source to reduce water to hydrogen over GCN photocatalysts is yet to be explored.

In the present paper, we report on the photocatalytic hydrogen evolution from aqueous solutions of hydrazine, unsymmetric dimethylhydrazine and hydrazinium sulfate under illumination with the UV light. Our results showed that for the GCN to be an efficient photocatalyst of water reduction it should be preliminary activated by a treatment with concentrated nitric acid.

#### 2. Materials and methods

Melamine (1,3,5-triaminotriazine), hydrazine hydrate, hydrazinium sulfate, unsymmetric dimethylhydrazine, concentrated HNO<sub>3</sub> (65 w.%) were purchased from Sigma-Aldrich and used without further purification. The nanocrystalline TiO<sub>2</sub> P25 was supplied by Evonik Corp.

#### 2.1. Preparation of GCN and acid treatment

The GCN was synthesized by the thermal condensation of melamine in air at a different temperature (further designated as  $T_s$ ) in the range of 450–600 °C and atmospheric pressure for 1 h in a quartz vessel similarly to [17]. The as-prepared samples were ground in a mortar and treated with the concentrated nitric acid. In a typical procedure of the acid treatment, 0.5 g GCN were immersed in 10 mL HNO<sub>3</sub> at room temperature and left with the magnetic stirring for a certain period of time further designated as  $t_{at}$  ( $t_{at}$  = 10 min–24 h). The sample was then washed with copious amount of distilled water till the neutral reaction, washed with 2-propanol and dried at 60 °C.

#### 2.2. Photocatalytic experiment

The process of photocatalytic hydrogen evolution was studied in glass cylindric thermostated reactors. In a typical experiment, a sample of GCN or  $TiO_2$  (0.02 g) was immersed into 10.0 mL aqueous solution of hydrazine or its derivatives and then a co-catalyst Pd/SiO<sub>2</sub> (0.01 g) was added to the reaction mixture. The co-catalyst (1 w.% palladium on commercial silica) was prepared by a chemical reduction method [18]. The suspension of a photocatalyst and the cocatalyst in aqueous solution of a donor (or a pure donor) was refluxed by a magnetic stirrer and illuminated with a high-pressure 1000 W mercury lamp light in the range of  $\lambda > 310$  nm and an intensity of 50 mW/cm<sup>2</sup>. The reaction mixture was evacuated prior to the illumination. The composition of the gas phase above the solution was determined each 30 min by the gas chromatography.

#### 2.3. Instruments

Diffuse reflectance spectra were registered on a Shimadzu UV-3600 spectrophotometer using BaSO<sub>4</sub> as a standard. The diffuse reflectance spectra were converted into absorption spectra using the Kubelka-Munk function and normalized for the convenience of comparison. X-ray Photoemission Spectroscopy (XPS) investigations were performed with an ESCALAB<sup>TM</sup> 250Xi X-ray Photoelectron Spectrometer Microprobe (Thermo Scientific). The X-ray photoelectron spectra were acquired under excitation of a 650  $\mu$ m<sup>2</sup> spot with the monochromatized Al K<sub> $\alpha$ </sub> X-ray source (hv = 1253.6 eV) providing a spectral resolution of 0.5 eV (pass energy of 20 eV) in high-resolution spectra. The survey XPS spectra were acquired with the pass energy of 200 eV. To prevent possible charging of the sample it was flooded with low kinetic energy electrons ( $E_{kin}$  = 0.1 eV,  $I_{em}$  = 0.05 mA). Spectra deconvolution and quantification were performed using the Avantage Data System (Thermo Scientific). The number of components used for each spectral decomposition was kept at the minimum required for a meaningful representation of the experimental spectra. A Voigt line shape was used to define the spectral shape of different components. Fourier-transform infrared (FTIR) spectra were registered using a Perkin Elmer Spectrum One spectrometer. The samples were prepared by pressing 15 mg of the sample with 100 mg KBr at 10 Mpa. X-ray diffraction patterns of the samples were registered on a Bruker D8 Advance diffractometer using the monochromatized copper  $K_{\alpha}$  irradiation ( $\lambda = 0.1540$  nm).

#### 3. Results and discussion

Our preliminary results showed that the as-prepared GCN does not exhibit any photocatalytic activity in molecular hydrogen evolution from aqueous solutions of hydrazine and its derivatives irrespectively of the temperature of GCN synthesis ( $T_s$ ). By analogy with previous reports [19–21], we tried to render the GCN photoactive by treating it with various chemical agents. The aqueous ammonia, hydrogen peroxide as well as the concentrated sulfuric and nitric acids were tested and it was found that a positive result can be achieved by bringing the powdered GCN into contact with the concentrated HNO<sub>3</sub> and such an activation way has not been reported yet for the photocatalytic systems based on the GCN. The photocatalytic activity of activated GCN (referred to as a-GCN in the following discussion) was found to depend both on the duration of the acid treatment  $t_{at}$  and the history of GCN preparation, in particular, the temperature  $T_s$  of melamine condensation.

#### 3.1. Kinetic aspects of the photocatalytic hydrogen evolution

Illumination of the samples of a-GCN dispersed in evacuated aqueous solutions of hydrazine hydrate (HH), hydrazinium sulfate  $N_2H_4 \times H_2SO_4$  (HS) or unsymmetric dimethylhydrazine  $H_2NN(CH_3)_2$  (DMH) in the presence of a Pd/SiO<sub>2</sub> co-catalyst results in the evolution of molecular hydrogen that proceeds with a constant rate (Electronic Supporting Information (ESI), Fig. S1). At the same time, no  $H_2$  can be detected in a similar system based on the untreated original GCN irrespectively of the parameters of its synthesis. Also, only traces of hydrogen form in the absence of Pd/SiO<sub>2</sub> indicating a crucial role of the palladium for hydrogen evolution with the participation of a-GCN. No  $H_2$  is evolved in the dark and

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under illumination in the absence of a-GCN and with only  $Pd/SiO_2$  present in the system. Also, only traces of hydrogen were detected in the absence of an electron donor ( $N_2H_4$  and its derivatives). All the facts indicate that hydrogen evolution is the result of photocatalytic water reduction with the participation of a-GCN as a light-absorbing species,  $Pd/SiO_2$  as a catalyst of dark stages and hydrazine and its derivatives as sacrificial electron donors.

Similar activation effects were also reported in the literature for the GCN treatment with other chemical agents. In particular, a twofold acceleration of the photoelectrochemical hydrogen evolution was observed in [19] after treatment of the GCN with concentrated HCl resulting in the protonation of the amine bridging groups connecting the heptazine blocks of the GCN. An enhancement of the photocatalytic water reduction was observed after a hydrothermal treatment of the GCN in the presence of ammonium thiosulfate [20]. Etching of the GCN with the ammonia resulted in a considerable increase of its photocatalytic activity in water reduction to molecular hydrogen [21]. At the same time no reports on using the concentrated HNO<sub>3</sub> to activate the GCN toward the photocatalytic water reduction could be found in the literature on the moment of the present paper preparation.

Fig. 1a shows the photoprocess rate achieved with various donors with a-GCN and TiO<sub>2</sub> Evonik P25, the latter used as a benchmark photocatalyst. The HH was found to be the least active electron donor and the a-GCN/HH-based system showed roughly twice lower efficiency of the hydrogen evolution as compared to the similar TiO<sub>2</sub>/HH-based system. The HS is a more active donor providing almost the same efficiency of hydrogen evolution both for a-GCN and TiO<sub>2</sub>. The photocatalytic H<sub>2</sub> evolution with the participation of a-GCN and DMH proceeds with the rate that is more than 4 times higher than that for the unsubstituted hydrazine. In the DMH-based system, the a-GCN is almost as active as TiO<sub>2</sub> P25, the latter typically showing superior photocatalytic activities in hydrogen evolution to most of the reported semiconductor photocatalysts. It should be also noted, that at elevated concentrations of donors, that is at a high pH, TiO<sub>2</sub> rapidly loses its activity while a-GCN remains stable and active (see discussion below).

We have varied basic parameters of the photocatalytic system such as a donor type and concentration, temperature, photocatalyst mass, light intensity as well as  $T_s$  and  $t_{at}$  to find the optimal conditions and to reach the maximal efficiency of the photocatalytic process.

#### 3.1.1. The light intensity and temperature

The rate of photocatalytic hydrogen production increases with an increase of the exciting light intensity in an almost linear manner throughout the studied range of up to 50 mW/cm<sup>2</sup> (ESI, Fig. S2a). The hydrogen evolution accelerates by a factor of around four with an increase of the temperature of the reaction mixture from 20 to 50 °C (ESI, Fig. S2b, curve 1). The temperature range was dictated by the leakage of vacuum grease at a higher T and the moisture condensation on the outer reactor walls at a lower T. An estimation of the activation energy basing on a linearization of the *R*<sub>H</sub>(T) dependence as ln(*R*<sub>H</sub>) vs 1000/T (ESI, Fig. S2b, curve 2) showed it to be as small as 25–30 kJ/mole. Such activation energy is typical for the photocatalytic H<sub>2</sub> evolution systems where limiting stages are formation and desorption of H<sub>2</sub> molecules from the co-catalyst surface [18].

#### 3.1.2. The photocatalyst and co-catalyst content

The dependences of  $R_{\rm H}$  both on the a-GCN and Pd/SiO<sub>2</sub> content are dome-shaped (ESI, Fig. S3). The rate of hydrogen evolution grows with an increase in the photocatalyst content, reaches a peak value at 0.02 g (per a 10-mL reactor) and then decreases (Fig. S3a). Similarly, the  $R_{\rm H}$  reaches a saturation value at an increase of the Pd/SiO<sub>2</sub> content to 0.0075–0.010 g and drops drastically at a

higher co-catalyst content–almost to zero in the presence of 0.04 g Pd/SiO<sub>2</sub> (Fig. S3b). Both dependencies originate most probably from the light shielding effect. At the photocatalyst content higher than 0.02 g the incoming light can be completely absorbed in a thin near-surface layer of the reactor while the rest of the reaction mixture remains unaffected by the light flux. In the case of Pd/SiO<sub>2</sub> that absorbs and scatters quite strongly the UV and visible light, an excessive loading of the co-catalyst can shield the reaction mixture from the incoming light thus decreasing considerably the efficiency of the photocatalytic process.

#### 3.1.3. The content of electron donors

The a-GCN exhibits a negligible photocatalytic activity in water reduction in the absence of any electron donors. As the HH or DMH is introduced into the system the hydrogen evolution begins and proceeds with a steady rate. The dependence of  $R_{\rm H}$  on the concentration of both donors is dome-shaped (Fig. 1b), the highest rate reached at around 12-14 M donor content in the case of HH (Fig. 1b, curve 1) and at 3-5 M in the case of DMH (curve 2). For the sake of comparison the rates of hydrogen evolution in the similar systems based on TiO<sub>2</sub> P25 is presented in Fig. 1b. As can be seen, the rate of photocatalytic hydrogen evolution is somewhat larger for the P25 at low donor concentrations. However, at a higher HH/DMH content the P25 titania rapidly loses its activity, most probably as a result of a pH increase, and at [HH, DMH] higher than 4 M TiO<sub>2</sub> is completely deactivated (Fig. 1b). In contrast, the a-GCN functions efficiently in such conditions and tolerates a further increase in the concentration of both donors retaining a reasonable photocatalytic activity even in the pure liquid HH and DMH (the cases correspond to [HH] = 20.4 M and [DMH] = 13.2 M, Fig. 1b). In the case of HS the rate of photocatalytic H<sub>2</sub> production grows with an increase in [HS], reaches a saturation value at [HS] > 0.1 M and does not change further (ESI, Fig. S4), the a-GCN and TiO<sub>2</sub> P25 revealing almost the same efficiency.

### 3.1.4. The synthesis temperature of original GCN and duration of the acid treatment

It was found that the temperature of the synthesis of original GCN that was used for the preparation of photocatalysts influences quite strongly the photocatalytic activity of the resulting a-GCN. The rate of H<sub>2</sub> evolution increases to some extent as a result of the T<sub>s</sub> elevation from 475 to 500 °C and decreases drastically at a higher synthesis temperature reaching at T<sub>s</sub> = 600 °C only around 10% of the *R*<sub>H</sub> observed at T<sub>s</sub> = 500 °C (Fig. 2a). The dependences of the same shape were obtained also for the HH and DMH (not shown).

The dependences of  $R_{\rm H}$  on the duration of post-synthesis GCN acid treatment are also similar for all three donors and reveal quite a sharp maximum at  $t_{\rm at} = 2$  h (Fig. 2b). A more prolonged contact with the concentrated HNO<sub>3</sub> results in a decrease of the photocatalytic activity of a-GCN. Such a dome-shaped dependence and a peak at  $t_{\rm at} = 2$  h were observed for the GCN samples synthesized at different temperatures.

### 3.2. The characterization of a-GCN samples and origins of the activation effect

The acid treatment of the GCN results in a "blue" shift of the fundamental absorption band edge, however, the shift magnitude does not correlate with the duration of the treatment. In the case of  $T_s = 500$  °C the band edge of original GCN can be observed at 440 nm (ESI, Fig. S5a, curve 1) corresponding to the band gap  $E_g$  of 2.82 eV. A 30-min contact with HNO<sub>3</sub> results in a band edge shift to 415 nm (Fig. S5a, curve 2,  $E_g = 2.99$  eV) and further treatment for 24 h only shifts the band edge to 410 nm (Fig. S5a, curve 4,  $E_g = 3.03$  eV). It can be concluded that the contact with HNO<sub>3</sub> results in a partial

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**Fig. 1.** (a) Rate *R*<sub>H</sub> of photocatalytic hydrogen formation in different systems. (b) Dependence of *R*<sub>H</sub> on HH (curve 1) and DMH concentration (curve 2). *Conditions*: 0.02 g a-GCN, 0.01 g Pd/SiO<sub>2</sub>, T = 20 °C. *Photocatalyst*: T<sub>s</sub> = 500 °C, *t*<sub>at</sub> = 2 h.



**Fig. 2.**  $R_{\rm H}$  as a function of temperature of the GCN synthesis T<sub>s</sub> (a) and duration of the acid treatment  $t_{\rm at}$  (b). Conditions: 0.02 g a-GCN, 0.01 g Pd/SiO<sub>2</sub>, [HS] = 0.2 M, T = 20 °C. Photocatalyst: in (a)  $t_{\rm at}$  = 2 h, in (b) T<sub>s</sub> = 500 °C.

destruction of the aromatic heptazine framework and a shrinking of the conjugation area with a corresponding increase of the interband electron transition energy [19,22,23]. However, the depth of such destruction for different  $t_{at}$  cannot be estimated from the optical absorption spectra.

The XRD pattern of starting GCN (ESI, Fig. S5b, curve 1) reveals two main peaks characteristic for the graphitic carbon nitride. The first peak at 27.3° reflects a layer-to-layer periodicity in the GCN with an interlayer distance of 3.26 Å, while the second one at around 13° corresponds to a periodicity between regular heptazine units within the single layers of carbon nitride (one of the most plausible structures of GCN single layer is provided in ESI, Fig. S6) with a period of 6.8 Å. The acid treatment of the GCN results in a considerable decrease of the intensity of both peaks (ESI, Fig. S5b, curve 2) and some shrinking of the interlayer distance to 3.22 Å. The changes indicate that the contact with HNO<sub>3</sub> results in a disruption of both periodic alteration of the single layers and the regularity within the GCN single layers [19,20,24,25]. However, as in the above case of optical absorption experiments, no clear dependence of the magnitude of such changes and the duration of the acid treatment can be discerned. It should also be mentioned that estimations of the thickness of the GCN and a-GCN particles made from the spectral width of the main XRD peak using the Scherrer equation showed that both values reside in a nanometer range changing from 6.5 nm for the original GCN to 4.8 nm for the a-GCN produced at  $t_{at} = 2$  h.

Scanning electron microscopy (SEM) images (ESI, Fig. S7) showed that the a-GCN ( $T_s = 500 \degree C$ ,  $t_{at} = 2 h$ ) consists of microscopic formations with a considerable portion of platelet-shaped particles. Many particles visible on the images reveal a lamellar periodic structure that most probably originates from the inherently layered character of a-GCN. The similar lamellar structure was also reported in [26] for the GCN produced at 500 °C via the condensation of melamine and cyanuric chloride. As suggested by XRD, the microscopic formations visible on the SEM images consist of smaller and much thinner platelets with the thickness of around 5 nm that cannot be resolved by SEM.

Such very thin a-GCN platelets can be observed by TEM (ESI, Fig. S8a,b) on the edges of large agglomerates that cannot be penetrated by the electron beam. The HRTEM images of separate platelets (ESI, Fig. S8c,d) showed the a-GCN platelets to be 5–6 nm-thick, in accor-

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dance with the XRD results, and exhibiting a layered structure with an interlayer distance of around 0.4 nm typical for the GCN.

It should also be noted that the TEM/HRTEM images of a mixture of a-GCN and Pd/SiO<sub>2</sub> presented in Fig. S8 (ESI) were taken after the completion of the photocatalytic test. No additional highercontrast (darker) spots can be observed on separate a-GCN platelets (Fig. S8a,b) that can be assigned to Pd nanoparticles indicating that no migration of palladium from the microcrystalline Pd/SiO<sub>2</sub> to a-GCN took place during the photoreaction as a result of possible Pd dissolution/photo-redeposition. Also, the examination of the mixure with SEM/EDX (ESI, Fig. S9) showed that palladium is only present on the high-contrast areas assigned to the Pd/SiO<sub>2</sub> beads and is not observed on other spots of the sample, thus confirming that no migration of Pd from the co-catalyst to the photocatalyst occurred during the photocatalytic process.

The original GCN produced at  $T_s = 500$  °C has a comparatively low specific surface area of  $10 \text{ m}^2/\text{g}$  as revealed by an analysis of the nitrogen adsorption/desorption isotherms (ESI, Fig. S10). The acid treatment of the GCN results in an increase of the surface area to 23, 36, and  $39 \text{ m}^2/\text{g}$  for the 2-h, 5-h, and 24-h treatment, respectively (Fig. S10). The a-GCN samples are, therefore, more disordered than the original GCN, in accordance with the XRD data, but have approximately the same specific surface area. The isotherms reveal a hysteresis indicating the presence of mesopores. The size of mesopores varies in the range of 20–30 nm indicating that the porosity of a-GCN samples originates from the inter-platelet voids rather than from the presence of real mesopores.

It was also found that the original GCN and the product of a 2-h acid treatment are characterized by almost identical FTIR spectra (ESI, Fig. S5c), which is also the typical situation for the thermally-treated [24,27] and chemically-treated GCN [19–21]. Taking into account the XRD, SEM and FTIR results we can only conclude that the structural changes in GCN introduced by the acid treatment occur mostly in the surface layer of the GCN particles and the concentration of the introduced defects (new functionalities) is low with respect to the overall GCN volume. By this reason, we subjected the a-GCN samples produced in different conditions to a study with the X-ray photoelectron spectroscopy which is a surface-sensitive method allowing to probe predominantly a thin surface layer of the GCN and a-GCN particles.

Survey X-ray photoelectron spectra of original GCN samples revealed two signals originating from carbon and nitrogen, and a low-intensity peak indicating the presence of oxygen admixture (ESI, Fig. S11). An atomic carbon-to-nitrogen ratio C/N was found to be 0.68 for all the untreated GCN samples (ESI, Table S1). The value is somewhat lower than that expected for the stoichiometric  $C_3N_4$ , C/N = 0.75, attesting to the presence of an excess of nitrogen and, therefore, to an incomplete character of the melamine condensation. The GCN samples reveal the presence of a small amount of oxygen, around 1%, incorporated into the carboxylic groups (see discussion below). The acid treatment of GCN in all cases results in an increase of the C/N ratio to 0.70–0.73, depending on T<sub>s</sub>. Simultaneously, the oxygen content increases from 1 to 3% after the acid treatment (Table S1). The observations indicate that the samples lose some nitrogen atoms and gain additional carboxylic groups as a result of the contact with HNO<sub>3</sub>. For each particular GCN the atomic C/N ratio increases in the first hours of the acid treatment, however, returns to the starting value after a more prolonged contact between the GCN and concentrated HNO<sub>3</sub> (see in ESI, Table S2 for the sample produced at  $T_s = 500 \circ C$ ). The oxygen content shows a steady increase as the acid treatment proceeds and reaches 4% after the 24-h acid treatment.

Examination of high-resolution X-ray photoelectron spectra in the characteristic range of N1s, C1s, and O1 s electron binding energies allowed to shed light on changes in the GCN structure produced by the contact with the concentrated nitric acid both as a function of  $T_s$  and  $t_{at}$ . The assignment of the components of C1s, N1s, and O1s bands was carried out using the reported XPS data pools [28,29] as well as the reports on the GCN photocatalysts activated by the thermal treatment [23,24,27] and chemical agents [19–21,25,30].

The N1s band in the X-ray photoelectron spectra of the untreated GCN samples (Fig. 3a) can be in all cases approximated by a combination of four components with maxima at 397.2 eV, 398.2 eV, 399.8 eV, and 403.3 eV. The first peak at 397.2 eV can be assigned to the binding energy of 1s electrons in the nitrogen atoms of C=N-C fragments of the heptazine cycles (pyridinic-N, highlighted by the blue color in Fig. S6, ESI). The feature at 398.2 eV is typically ascribed to the nitrogen atoms bound with three C atoms in the heptazine heterocycles (NC<sub>3</sub> fragment). In a broadly accepted model of a GCN single layer such atoms can be found in the center of heptazine heterocycles (highlighted by the green color in Fig. S6, ESI). The peak at 399.8 eV can be assigned to the nitrogen atoms in -NH- and -NH<sub>2</sub> fragments of GCN (highlighted by the red color in Fig. S6, ESI). A broad band at 402-407 eV is typically assigned to plasmon excitation of the aromatic system of heptazine heterocycles.

The C1s band of the GCN samples can be deconvoluted into four separate components peaked at 284.5 eV, 287.8 eV, 288.8 eV, and 293 eV (Fig. 3b). The most intense peak at 287.8 eV is characteristic for aromatic carbon in the heptazine heterocycles (N=C–N fragments). The peak at 284.5 eV corresponds to the 1s electron binding energy in the carbon atoms of single C–C bonds (sp<sup>3</sup>-C) originating from aliphatic residuals and adventitious carbon (absorbed by the samples from the environment). The low-intensity peak at 288.8 eV is typical for the carbon atoms in carboxylic groups. Similarly to the N1s series, the broad band peaked at 293 eV is ascribed to plasmon excitation of the heptazine heterocycles.

Each GCN sample revealed also a low-intensity O1s band that combines two components with maxima at 530.3 eV and 531.4 eV (Fig. 3a, insert) typical for oxygen atoms in C–O and C=O groups, respectively.

Relative contributions of the above-discussed components into the N1s and C1s bands were calculated as a ratio of the area of the selected components to the integral area of the N1s, C1s or O1s bands for a given sample (ESI, Table S3). The major part of nitrogen atoms (~70%) in the original GCNs belong to the C=N–C groups. A minor portion of the nitrogen atoms (~20%) occupies central positions in the heptazine heterocycles binding to three neighboring carbon atoms. Around 10% of the nitrogen atoms belong to the bridging C<sub>2</sub>NH groups that connect heptazine cycles and form the infinite poly heptazine chains (ESI, Fig. S6). A major part of the carbon atoms in the GCN sample (~93%) belongs to the heptazine heterocycles. Besides, the sample reveals the presence of adventitious carbon (~5%) and a very small amount of carboxylic/carbonyl groups that can be regarded as point defects in the poly heptazine structure.

It was found that even a relatively short, 0.5 h, contact of the GCN with the concentrated HNO3 results in considerable changes in the sample structure (ESI, Table S3) that become more pronounced at a longer acid treatment (Fig. 3c,d). In particular, a decrease of the relative contribution of pyridinic-N from 70% to 56% and a corresponding increase of the relative content of nitrogen in NC<sub>3</sub> fragments from 20% to 34% can be observed. A more prolonged acid treatment results in a further decrease of the relative content of the pyridinic nitrogen - down to 48% for the 24-h contact with the nitric acid. These observations are in accordance with the analysis of the C1s series indicating that the acid treatment induces a decrease of the relative content of the aromatic carbon from 93% in the untreated sample to 81% for the a-GCN sample contacting with the acid for 24 h. Simultaneously, an increase in the relative content of carbon atoms bound in the carboxylic groups is observed- from 2% for the original GCN to 15% for the a-GCN sample produced by the

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**Fig. 3.** High-resolution X-ray photoelectron spectra of GCN (sections a, b) and a-GCN (sections c, d) in the range of N1s (a, c) and C1s (b, d) electron binding energy. Insert in (b): O1s XPS band of a-GCN sample. *Preparation conditions*: T<sub>s</sub> = 500 °C, t<sub>at</sub> = 2 h.

24-h acid treatment. At that, the relative contribution of the adventitious carbon ( $sp^3$ -C) remains low and almost steady, around 5%. Therefore, the XPS results show that interaction of the GCNs with nitric acid results in a partial destruction of the heptazine heterocycles of the GCN single layers in the near-surface area of the samples with a decrease of the nitrogen content and formation of structural defects. One of the possible defects detected by the XPS is the carboxylic group. Similar effects were observed in [24] to be produced by a thermal treatment of the GCN at 660 °C. The formation of structural defects was supposed to be the reason for an increase of the photocatalytic activity of the treated GCN in water reduction and Rhodamine B decomposition [24] as well as N<sub>2</sub> reduction [27].

A relative content of different structural units for a series of the GCN samples produced at a different  $T_s -$ from 475 °C to 600 °C as well as for the corresponding a-GCNs ( $t_{at} = 2$  h) is provided in ESI (Table S4). The untreated GCN samples are characterized by a different oxygen content and by some differences in the content of aromatic carbon and the two-coordinated nitrogen. In particular, the fraction of pyridinic nitrogen increases from 53% to 70% at an elevation of the  $T_s$  from 475 to 500 °C and decreases at a higher temperature – down to 51% for  $T_s = 600$  °C. In a similar manner, the maximal relative content of the aromatic carbon in the studied series, 93%, is observed for the GCN sample produced at 500 °C. At the same time, an increase of  $T_s$  from 475 °C to 600 °C results in an increase of the relative content of the carbon atoms bound to the oxygen atoms- from 2% for  $T_s = 475-500$  °C to 8% for the GCN sample synthesized at 600 °C.

The acid treatment of all the samples results in changes in their structure that show a similar trend. In particular, we observed a decrease of the relative contribution of the pyridinic nitrogen and an increase in the relative content of the NC<sub>3</sub> fragments, as well as a decrease in the relative contribution of the aromatic carbon and an increase of the population of the carbon atoms bound to oxygen (ESI, Table S4). The latter trend is most vividly pronounced for the GCN sample produced at 500 °C, where the acid treatment results in an increase of the relative carbon content in the C–OH/C=O fragments from 2 to 7%. We can conclude, therefore, that an increase in the temperature of GCN synthesis from 500 °C to 600 °C and the post-synthesis acid treatment of the sample produced at T<sub>s</sub> = 500 °C

result in similar changes, that is, in a partial destruction of the heptazine heterocycles with the elimination of the C–N=C fragments and the formation of various structural defects, in particular, nitrogen vacancies and carboxylic groups. The post-synthesis acid treatment of such defect-enriched samples results in the formation of additional defects in the structure of GCN samples.

Summarizing, the XPS results show that the photoactivity of a-GCN originates most probably from new structural defects introduced by the acid treatment. The chemical nature of the defects can be versatile and a particular sort of defects that can be observed by XPS is the carboxylic groups, but a contribution of other species cannot be ruled out. The defects can apparently serve as traps for the photogenerated charge carriers slowing down their recombination and allowing for the more efficient interfacial charge transfer to the reactants to occur. Most probably, as is the case for inorganic semiconductor photocatalysts, the structural defects can also participate in the recombination processes. Therefore, an optimal defect density exists yielding the maximal photocatalytic activity, while at a higher concentration of defects the recombination processes prevail and the photoactivity of a photocatalyst deteriorates.

In the case of GCN, which is characterized by a complex structure (molecular polyheptazine units constituting infinite sheets where a periodic potential for the photogenerated charges is created) and a versatility of possible defects, the introduction of a new defect can either guench PL or, in some cases, result in the PL enhancement. For example, we have recently reported on the PL properties of GCN produced at different condensation temperature [31] and found that the higher is the synthesis T, the lower is the PL intensity of GCN as a result of the formation of additional defects during the thermal treatment. However, after the exfoliation of the GCN to single-layer and a-few-layer sheets this dependence has reversed - the exfoliation products of GCN produced at a higher T revealed a higher PL efficiency reflecting a versatility of defects that can participate in radiative processes and a strong influence of the environment of the photophysical processes in GCN. Also, it is widely reported for the graphene quantum dots and carbon nanoparticles that the introduction of additional hydroxyl/carboxyl groups to their basal plane or surface, respectively, results in an enhancement of fluorescence [32]. So, the COH/COOH groups can act in these cases not only as

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point defects capable of charge trapping but also as additional sites of radiative recombination.

A direct evidence of the increased charge trapping by shallow traps of the a-GCN can be found in photoluminescence (PL) measurements (ESI, Fig. S12). The acid treatment results in a considerable growth of the PL intensity even at early stages of the acid treatment (the first 10 min). However, at a more prolonged acid treatment, the PL intensity remains steady and almost does not vary with the treatment time. At the same time, at a certain treatment duration, around 2 h and longer, the photocatalytic activity also reaches a saturation level and further generation of the defects only enhances the radiationless recombination thus resulting in a decrease of the photocatalytic activity.

A similar situation is most probably realized by the variation of the synthesis temperature. Formation of structural defects by annealing of the GCN both in the air and in an inert atmosphere is a well-reported way of influencing the photocatalytic properties of GCN [24,26,27]. In particular, thermal activation of the GCN as a photocatalyst of hydrogen evolution observed in [22,23,26] was mainly ascribed to the generation of structural defects.

With an increase of  $T_s$  in the range of 500–650 °C, the density of structural defects in the GCN is expected to increase as well. We can, therefore, anticipate that the introduction of the defects makes the GCN more susceptible to the attack of the nitric acid and the following acid treatment should produce more additional defects for the samples synthesized at a higher temperature which is in accordance with the XPS data. As a result, we observe the dome-shaped dependencies of the hydrogen evolution rate both on the acid treatment duration and the synthesis temperature of the starting GCN samples with the peaks at  $t_{at} = 2$  h and  $T_s = 500$  °C.

#### 4. Conclusion

The graphitic carbon nitride treated with the concentrated nitric acid revealed a photocatalytic activity in hydrogen evolution from aqueous solutions of hydrazine, unsymmetric dimethylhydrazine and hydrazinium sulfate in the presence of a Pd/SiO<sub>2</sub> co-catalyst. The rate of photocatalytic water reduction was found to be maximal in the presence of 3-5 M DMH and 12-14 M hydrazine hydrate and comparable to the hydrogen evolution rate in similar systems based on titania Evonik P25. However, in contrast to TiO<sub>2</sub>, the activated GCN retains photocatalytic activity at higher concentrations of electron donors and can operate even in the pure liquid hydrazine hydrate and DMH while the TiO<sub>2</sub> P25 is completely deactivated in such alkaline media.

The rate of photocatalytic hydrogen evolution from aqueous solutions of hydrazine and its derivatives was found to depend on the duration of the treatment with the nitric acid  $t_{at}$  as well as on the GCN synthesis temperature T<sub>s</sub>. Dependences of the photoprocess rate on  $t_{at}$  and T<sub>s</sub> are dome-shaped with maxima at  $t_{at}$  = 2 h and T<sub>s</sub> = 500 °C.

An X-ray photoelectron spectroscopic study revealed that the GCN acid treatment results in the elimination of some of the nitrogen atoms in the heptazine building blocks of GCN and formation of carboxylic groups. The amount of introduced defects and oxygencontaining groups increases with an increase of both *t*<sub>at</sub> and T<sub>s</sub>. The GCN activation effect induced by the acid treatment was supposed to originate from the participation of the introduced defects/COOH groups in the trapping and interfacial transfer of the photogenerated charge carriers.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2016.12. 024.

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