High surface area, spongy graphitic carbon nitride derived by selective etching by Pt and Ru nanoparticles in hydrogen

Emilia Alwin¹, Michał Zieliński¹, Agata Suchora¹, Iwona Gulaczyk¹, Zbigniew Piskuła¹, and Mariusz Pietrowski¹,*

¹Faculty of Chemistry, Adam Mickiewicz University, Poznań, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland

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ABSTRACT

It was observed for the first time that the specific surface area of graphitic carbon nitride (g-C₃N₄) increased from 32 m²g⁻¹ to 142 and 171 m²g⁻¹ for Pt and Ru, respectively, due to the etching of g-C₃N₄ by Pt and Ru nanoparticles. Metal nanoparticles catalyze hydrogenation of C – N bonds and “move” through the structure of g-C₃N₄ etching tunnels in it and creating “spongy graphitic carbon nitride” (sgCN). The reactions take place on the surface of metal NPs, which are covered with oxidized forms of Pt and Ru capable of strong interactions with nitrogen, which was confirmed by XPS studies. The activation energy of hydrogenation of g-C₃N₄ is 112 and 151 kJmol⁻¹ for Ru and Pt nanoparticles, respectively. The process of etching of g-C₃N₄ was observed by mass spectrometry and temperature programmed reduction coupled with on-line infrared spectroscopy. On the basis of thermodynamic considerations and quantum mechanical calculations of bonds strengths, a probable mechanism of g-C₃N₄ hydrogenation was proposed.
Introduction

Liu and Cohen [1] predicted that carbon nitride may show very promising properties as a superhard material—harder than diamond. Then, in 2009 Wang et al. discovered some unusual photocatalytic properties of graphitic carbon nitride (g-C₃N₄) [2]. Graphitic carbon nitride is a layered material—just like graphite. The layers are created by tri-s-triazine (heptazine) units connected through a tertiary nitrogen atom; layers between each other are connected by hydrogen bonds [3]. Because of its layered structure, g-C₃N₄ can be subject to delamination/exfoliation (just like graphite). Owing to this, its specific surface area (SSA) can be increased. Using traditional methods of synthesis by thermal condensation of urea, thiourea, dicyandiamide or melamine, the specific surface area of g-C₃N₄ is 10–30 m²g⁻¹ [4–6]. The limitation of carbon nitride is just its low SSA. In a number of potential applications such as photo-, electro-, heterogeneous- catalysis, and gas storage, a high SSA is essential. Hence, attempts were made to synthesize the high-surface area of g-C₃N₄ by using hard or soft template methods [7–10], by exfoliation into nanosheets [11–14] or by heteroatom doping [15, 16]. The most commonly used method is the hard template method based on the use of high-surface area inorganic material, which acts as the matrix on which g-C₃N₄ is synthesized. After removing the matrix, a negative copy of the used matrix is obtained. Goettmann et al. [7] obtained mesoporous g-C₃N₄ with a surface reaching 440 m²g⁻¹ by using colloidal silica nanoparticles as a template. Using SBA-15, g-C₃N₄ was obtained with ordered, 2D hexagonal porosity and SSA reaching 239 m²g⁻¹ [8]. Similar effects are observed by the soft template method—carbon nitrides obtained by this method reach SSA of 134 m²g⁻¹ [9] or 220 m²g⁻¹ [10]. Using the layered structure of carbon nitride and experience in exfoliation of graphite to graphene, g-C₃N₄ was subjected to similar treatments many times. For instance, exfoliation in concentrated sulfuric acid under ultrasonication allowed Lee et al. [11] for an increase in SSA of g-C₃N₄ from 20 to 140 m²g⁻¹ while Gao et al. [14] to 199 m²g⁻¹. Apart from chemical methods of exfoliation, thermal exfoliation is also applied. It allows for an increase in SSA of g-C₃N₄ to 150 m²g⁻¹ [13] and sometimes even (repeating exfoliation three times) to 513 m²g⁻¹ [12]. However, it should be pointed out that the final product yield did not exceed 6% in the latter case. The third group of methods used to increase SSA is doping of g-C₃N₄ by heteroatom. Zhu et al. [15]...
obtained phosphorus-doped graphitic carbon nitride nanostructured flowers of in-plane mesopores with surface of 83 m² g⁻¹. Sometimes combining several methods described above gives excellent results. Thus, Zhao et al. [17] applying SBA-15 as hard template and hexamethylenetetramine as carbon nitride precursor obtained highly ordered mesoporous carbon nitride nanorods with 971–1124 m² g⁻¹ of super-high specific surface area.

The methods discussed above are usually laborious, often expensive and ineffective; therefore, alternative methods are still being sought.

In the 1970s, Tomita et al. [18, 19] carried out research on the hydrogenation of carbons and discovered that metal nanoparticles etch the channels on the surface of graphite [20]. Later, this phenomenon was observed many times for a few layers of graphene on a number of metals, such as Ni, Co, Fe, Ag, and W [21–29]. It turns out that nanoparticles of Ni etched not only the surface of highly oriented pyrolytic graphite, but also the network of tunnels throughout its volume, generating a porous form of graphite [26]. Thus, it is possible to transform non-porous (or low-porous) material into mesoporous material that consists of cylindrical pores. The only alternative to this method is the nanocasting method, which leads to mesoporous g-C₃N₄ too, but by its nature is time consuming and laborious, and usually requires expensive templates [17, 30–32].

In this work, the phenomenon of etching channels by metal nanoparticles was applied to create pores in the structure of g-C₃N₄ and increase its SSA. Since the etching of carbon materials is based on a hydrogenation process, platinum and ruthenium were chosen as metals of high hydrogenation activity.

Experimental

Materials and methods

Graphitic carbon nitride (g-C₃N₄) was obtained by pyrolysis of dicyandiamide (DCDA) (Sigma-Aldrich, 99%). 4 g of DCDA was placed in a 50 mL quartz crucible, covered with a lid, and heated in a muffle furnace for 4 h at the temperature of 600 °C (heating rate of 10°C min⁻¹). The crucible was left in the oven to cool to room temperature. The obtained canary-colored g-C₃N₄ was ground in an agate mortar to a fine powder. The sample was denoted with the symbol gCN.

H₂PtCl₆ from water solution and Ru₃(CO)₁₂ from methanol solution were introduced onto a surface of the obtained gCN using the wet impregnation method. The amount of chloroplatinic acid and ruthenium dodecacarbonyl was adjusted to obtain 1.0 wt% of Pt and Ru on g-C₃N₄. gCN was contacted with the metal precursor solution for 2 h on a magnetic stirrer. The solvent was evaporated on a rotary evaporator. The samples were dried overnight at 80 °C. Catalyst samples and of gCN were stored in a desiccator over molecular sieves 4A. The catalysts were marked with the symbols Pt/gCN and Ru/gCN.

gCN and metal catalysts (in a dried form) were reduced at 525 °C in a tube furnace in a hydrogen flow (50 mL min⁻¹), with a heating rate of 10°C min⁻¹. The reduced gCN was marked with the symbol gCNR while the catalysts with the symbols Pt/gCNR and Ru/gCNR.

Characterization of the samples

The specific surface area (SSA) was determined by Brunauer–Emmett–Teller (BET) method, while the total pore volume and average pore diameter were calculated using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of isotherms using a Micromeritics ASAP 2010 surface area and porosity analyzer (from N₂ adsorption isotherms collected at 77 K).

The elemental analysis was investigated on Flash 2000 exhaust-gas analyzer (Thermo Fisher Scientific, Waltham, MA, USA) by combustion on 900–1000 °C.

An FEI Helios NanoLab 660 (Thermo Fisher Scientific, Waltham, MA, USA) electron microscope was used to obtain SEM images.

The powder X-ray diffraction patterns of the samples were obtained using a Bruker D8 Advance diffractometer by using CuKα radiation. The XRD data were collected over a 2θ range of 10–35° with a step size of 0.01° and the scanning time rate of 5 s.

XPS measurements were made with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK). The excitation source was a monochromatized aluminum X-ray source (Al Kα (1486.6 eV) operated at 10 mA and 15 kV. The charge referencing method used was the C (C, H) component of the C 1 s peak of adventitious carbon fixed at 284.8 eV. Spectroscopic data were processed by the CasaXPS ver. 2.3.17PR1.1 software (Casa Software Ltd., UK), using a peak-
fitting routine with Shirley background and asymmetrical Voigt functions.

The Pt and Ru content were evaluated by the inductively coupled plasma (ICP) method. For ICP analysis, 15 mg of a sample (reduced at 300 °C) was added to an aqua regia solution for Pt and a mixture of H2SO4, aqua regia, and HF for Ru. The mixture was then autoclaved at 110 °C for 2 h. The digested solution was diluted with ultrapure water and analyzed for ICP by Agilent 720-ES ICP-OES. Measurements had showed that the content of Pt and Ru in the samples were 0.86 and 0.80 wt%, respectively.

**Temperature programmed reduction measurements—hydrogen consumption and evolved gases analysis**

The temperature-programmed reduction technique using the ASAP ChemiSorb 2705 instrument was applied to analyze the changes appearing in g-C3N4 during heating in hydrogen. A sample of ~10 mg was placed in a U-shaped quartz vessel and reduced in a mixture of 10 vol% H2 in Ar (99.999%, Linde) at a flow of 30 mL min\(^{-1}\) and heated with a rate of 10°C min\(^{-1}\). Hydrogen consumption was measured using thermal conductivity detector (TPR-TCD). In order to calculate the amount of consumed hydrogen, the TCD signal was calibrated by injecting 1054 µL portions of hydrogen into a flowing argon stream using a gas loop. All results were normalized to the same sample weight.

The identification of gaseous products of etching of gCN and metal/gCN samples was conducted using a gas analyzer ThermoStar made by Pfeiffer, model GDS301T2 with an analyzer QMA200 M, which was connected directly to the TPR instrument. The identification of fragmentation ions was carried out using the National Institute of Standards and Technology database (NIST) [33] and [34–36]. In the gas products of the metal/gCN catalyst reduction, the following ions were identified, those of \(m/z = 12, 13, 14, 15, 16\) assigned to the fragmentation of CH\(_4\) [34], those of \(m/z = 14, 15, 16, 17\) assigned to NH\(_3\) [35, 36], and those of \(m/z = 12, 13, 14, 26, 27, 28\), evidencing the presence of HCN [36]. Moreover, the spectra showed the ions coming from hydrogen and argon (components of the reducing mixture), small amounts of H2O and traces of air from the surroundings.

Quantitative analysis of the released methane, ammonia and hydrogen cyanide was performed using infrared spectrometer FTS 3000 Bio-Rad (Bio-Rad, CA, USA) coupled with the TPR instrument (TPR-IR). The gases released from the TPR apparatus were directed to a gas cuvette equipped with NaCl windows. The optical path of the cuvette was 20 cm and its total volume was 15 mL. Such a small volume of the cuvette allows for a quick gas exchange (within 3–5 min) as the total gas flow rate during TPR measurement was 30 mL min\(^{-1}\).

Based on the FTIR spectra the plots presenting the dynamics of gas evolution were generated. For this purpose, the absorbance of characteristic bands was determined at: 2850–3180 cm\(^{-1}\) for methane, 780–1180 cm\(^{-1}\) for ammonia, 625–790 cm\(^{-1}\) for hydrogen cyanide. Having the maximum intensity of the band and using the Lambert–Beer law, the concentration of individual components was determined taking the absorbance cross-section (in cm\(^2\) mol\(^{-1}\)) from Pacific Northwest National Laboratory (PNNL) quantitative database containing the vapor-phase infrared spectra of pure chemicals) [37],
\[
\begin{align*}
\text{CH}_4 & = 1.87 \times 10^{-18}, \\
\text{NH}_3 & = 2.87 \times 10^{-18}, \\
\text{HCN} & = 3.6 \times 10^{-18}
\end{align*}
\]

On this basis, the charts were plotted showing quantitatively the dynamics of methane, ammonia and hydrogen cyanide release during the reduction/etching of gCN and metallic catalysts.

On the basis of the TPR-TCD curves, the activation energy of reduction in g-C3N4 was determined. The TPR-TCD curve is a differential curve showing hydrogen consumption (Fig. S3a). The curve was converted to a cumulative plot of hydrogen consumption (Fig. S3b), which illustrates the degree of decomposition of a sample \(x\) (Fig. S3c). The graphical method developed by Coats and Redfern (Fig. S3d) was used to evaluate activation energy (\(E_a\)) from TPR-TCD curves [38].

Gas phase thermochemistry data (\(\Delta H_{298}^\circ \) and \(G_{298}^\circ \)) for methane, ammonia and hydrogen cyanide was taken from the NIST database (National Institute of Standards and Technology) [39, 40] and for g-C3N4 from Kuntz and Deutschmann [41].

**Quantum–mechanical calculations**

In order to calculate the energy bond of particular bonds in g-C3N4, calculations were performed in Gaussian16W [42]. Since the aim of these calculations was to estimate the energy bonds for the conceptual mechanism of the g-C3N4 decomposition, the simple Hartree–Fock method (HF method) only was used
with two basis sets of 3-21G and 6-311G(d). The final results of energy bonds presented in this work are calculated with a basis set 6-311G(d).

**Results and discussion**

**Synthesis and physicochemical characterization of spongy g-C$_3$N$_4$**

Graphitic carbon nitride was obtained by thermal condensation of dicyandiamide (DCDA) at 600 °C for 4 h and was denoted as gCN [43, 44]. In Fig. 1a, low-temperature nitrogen adsorption/desorption isotherms of the samples are presented. The specific surface area of gCN is 32 m$^2$g$^{-1}$ (Table 1) and is close to the values obtained by other researchers [45, 46]. gCN was reduced at 525 °C in hydrogen flow for 2 h (denoted as gCNr); SSA increased to 43 m$^2$g$^{-1}$. The increase in the SSA of g-C$_3$N$_4$ after heating in hydrogen was observed earlier by Maschmeyer et al. [47] and was assigned to the delamination of g-C$_3$N$_4$ to nanosheet (after H$_2$ treatment at 550 °C) [48]. On the other hand, Niu et al. [48] claimed that reduction in g-C$_3$N$_4$ in hydrogen at 540 °C leads to the elimination of amino groups and forms nitrogen vacancies, which, however, do not change the crystal structure of g-C$_3$N$_4$. The low temperature N$_2$ adsorption isotherms for gCN and gCNr (Fig. 1a) belong to type IV and the hysteresis loop to type H3, which is characteristic for plate-like particles giving rise to slit-shaped pores. Ru(CO)$_{12}$ and H$_2$PtCl$_6$ were deposited on the surface of gCN by the impregnation method and reduced. The shape of adsorption/desorption nitrogen adsorption isotherms for the reduced systems of Pt/gCNr and Ru/gCNr are of type H1, which indicates the presence of cylindrical-like pore channels, and SSA increases to 142 and 171 m$^2$g$^{-1}$ for Pt and Ru catalysts, respectively (from initial 32 m$^2$g$^{-1}$ for gCN). The increase in the SSA of metal catalysts is accompanied by an increase in total pore volume and a decrease in average pore diameter (Table 1).

Porosity analysis shows that Pt and Ru nanoparticles (NPs) in the presence of hydrogen induce changes in the structure of g-C$_3$N$_4$ leading to a significant increase in SSA. We believe that this increase in SSA is the result of catalytic hydrogenation and

![Figure 1](image-url)
hydrogenolysis of C–N bonds in carbon nitride by metal NPs, and not of the delamination of g-C3N4 to a nanosheet structure as stated in a paper by Maschmeyer et al. [47], which can be proved by the shape of the adsorption isotherm, characteristic of cylindrical-like pores. Metal nanoparticles like a Pac-Man from a famous computer game in the 1980s, nibbled g-C3N4 etching channels/tunnels in its structure. The phenomenon of etching channels by metal nanoparticles has been observed many times in pure carbon materials, mainly graphite and graphene [22, 23, 25, 26, 28, 29, 49], but never before for carbon nitride. In one recent paper [50], the term “Pac-Man mechanism” was used to describe this phenomenon, which seems to be very apt. In this context, the question of the size of metal NPs arises. The metal precursor was introduced onto the g-C3N4 surface by the impregnation method. After evaporating the solvent and drying the sample, it was reduced in a hydrogen flow from RT to 525 °C. During the temperature rise, the precursor is reduced first and metallic NPs are formed (Fig. S1). The reduction process of Pt and Ru precursors is completed below the temperature of 300 °C. Such catalysts (reduced at 300 °C) were described in our earlier work [51]. The resulting Pt and Ru crystallites had a size of 2.1 i 2.3 nm, respectively. We believe that such crystallites nibbled g-C3N4 etching channels/tunnels in its structure.

Powder X-ray diffraction tests were conducted to observe the changes of the crystal structure of carbon nitride (Fig. 1b). In the diffraction pattern of gCN, which like graphite is a layered-built material, a characteristic reflex is present at 27.75°2θ, corresponding to an interlayer spacing of 3.21 Å. After reduction in pristine gCN in hydrogen, a slight shift of reflex is recorded to smaller angles (to 27.65°2θ), which indicates an increase in interlayer spacing (d = 3.22 Å), which is probably related to the delamination of g-C3N4 as observed by Maschmeyer et al. [47]. However, in metal catalysts, the intensity of the reflex 27.75°2θ is clearly lowered, which proves a partial destruction of the gCN structure during the reduction at 525 °C. Simultaneously, changes caused by Ru NPs are greater than by Pt NPs. We believe that this is related to the hydrogenation activity of both metals; Ru is known for its high activity in hydrogenation of the C–N bond [52, 53]. This is confirmed indirectly by the results of elemental analysis (Table 1); the C/N atomic ratio is the highest for Ru/gCNr catalysts and is equal to 1.04 (summary formula C3N2.9), whereas for Pt/gCNr it is 0.88 (summary formula C3N3.4), which can prove that nitrogen is preferred to be eliminated by ruthenium from the structure of g-C3N4.

Table 1 Results of low-temperature nitrogen adsorption measurements (SSA, average pore diameter, total pore volume) and elemental analysis measurements

| Sample  | SSA (m2 g−1) | Average pore diameter (nm) | Single point total pore volume (cm3 g−1) | Elemental analysis |
|---------|--------------|----------------------------|-----------------------------------------|-------------------|
| gCN     | 32           | 15.1                       | 0.12                                    | C3N4.5            |
| gCNr    | 43           | 11.9                       | 0.13                                    | C3N4.3            |
| Pt/gCNr | 142          | 8.2                        | 0.29                                    | C3N3.4            |
| Ru/gCNr | 171          | 7.3                        | 0.31                                    | C3N2.9            |

In Fig. 2, the SEM images of gCN and Ru and Pt catalysts after reduction in hydrogen at 525 °C for 2 h are presented. The SEM images showed no effect of the reduction on the structure of pristine gCN. Contrary to this, the structure of metal catalysts is significantly different from that of gCN. The surface of the catalysts resembles a porous sponge (pumice), hence the materials obtained can be called “spongy graphitic carbon nitride” (sgCN). We think that metal nanoparticles “migrate” in the structure of carbon nitride etching channels/tunnels in it, as was observed in the case of graphite [20, 26, 54, 55], graphene [21, 22, 24, 25, 27–29, 50], and recently for boron nitride [56].

X-ray photoelectron spectroscopy (XPS) is one of the most sensitive surface analysis methods for revealing information about the chemical state of elements in a sample. XPS is also commonly used to study the structure of graphitic carbon nitride. Figure 3a shows the C 1s core-level XPS spectra for the gCN, gCNr, Pt/gCNr, and Ru/gCNr samples. Two
basic bands can be distinguished in the C 1 s spectrum of carbon nitride: first at 284.8 eV derived from graphitic carbon (C−[C,H] adventitious carbon, AdC), which was used for energy calibration, and second at ~288.2 eV assigned to sp²-bonded carbon (N=C=N) in the heptazine rings [43] (denoted as Py – pyridinic carbon). The spectra also show a small band from nitrile species –C≡N [57, 58], which is sometimes observed for g-C₃N₄ synthesized at high temperatures [43]. Changes in the g-C₃N₄ spectrum after reduction (gCNr) are negligible and amount to a slight decrease in its intensity. On the other hand, the spectra of systems containing platinum and ruthenium are clearly evolving. Two main effects are observed: (1) a decrease in the intensity of the Py band indicating the progressive degradation of the C−N=C bonds in the g-C₃N₄ heptazine subunits, (2) the appearance of a new band at 284.2 eV, which can be assigned to the so-called defective carbon and should be considered as point defects in the graphite lattice [59, 60]. Both of these phenomena (degradation of the heptazine structures and the appearance of a new form of carbon) lead to an increase in the C/N ratio, which was 0.80 for gCN and 1.13 and 2.36 for Pt/gCNr and Ru/gCNr, respectively (Table S1). The increased C/N ratio in metallic systems was demonstrated by the results of elemental analysis presented earlier (Table 1). The above results show that during the reduction in the metal/gCN systems, the destruction of the heptazine subunits and elimination of carbon and nitrogen occur with the increase in the C/N ration due to the decrease in nitrogen—part of the carbon remains in the sample in the form of defective graphite-like structures.

Figure 2 SEM micrographs of the gCN, gCNr, Pt/gCNr and Ru/gCNr samples (1 wt%).
Figure 3b presents the N 1 s core-level XPS spectra. There are four characteristic bands at 398.6, 399.4, 400.3 and 401.2 eV assigned to pyridinic nitrogen in the heptazine ring (denoted Py), nitrogen in amino group (NH₂), nitrogen in imino group (NH), and quaternary nitrogen originating from the N–(C)₃ component (Q), respectively [43, 61]. As in the C 1 s spectrum, the difference between gCN and gCNr is...
minimal. Much greater changes in the structure of g-C₃N₄ are generated in the presence of Pt and Ru. The intensities of the Pt/gCNr and Ru/gCNr spectra drop significantly. It should be noted that the decrease is considerably greater for ruthenium than for platinum and it affects all the forms of nitrogen to a comparable degree (Table S2). That means that all the forms of nitrogen (Py, NH₂, NH, Q) are eliminated from the g-C₃N₄ structure to a comparable extent.

The XPS technique also allowed us to observe the surroundings and oxidation degree of platinum and ruthenium. The XPS spectrum of the Pt 4f region of the Pt/gCNr sample is shown in Fig. 3c. There are three doublets in the spectrum. The first doublet at 70.8 and 74.2 eV corresponds to the 4f₇/₂ and 4f₅/₂ states of Pt⁰, respectively. The second doublet at 73.5 and 76.9 eV corresponds to the 4f₇/₂ and 4f₅/₂ states of platinum (II) coordinated to nitrogen atoms, respectively [51, 62–65]. Finally, the doublet at 76.7 and 79.1 eV corresponds to platinum (IV), also coordinated to nitrogen atoms [66, 67]. Most of platinum (71.1%) forms metallic crystallites while the rest appears in the nitrogen-coordinated oxidized form.

Ru 3p core-level XPS spectrum of Ru/gCNr sample is shown at Fig. 3d. The presence of metallic ruthenium is evidenced by the doublet at 461.1 and 483.6 eV for 3p₃/₂ and 3p₁/₂ states of Ru⁰, respectively [68]. The doublet at 466.1 and 488.3 eV derives from nitrogen-coordinated oxidized forms of ruthenium [69–71]. Finally, a doublet at 462.8 and 485.0 eV with a doublet separation of 22.2 eV originates from RuO₂ [68], which is confirmed by the peak observed at 529.4 eV with satellite at 531.2 eV in the O 1 s spectrum (Fig. S2). The presence of platinum oxides was excluded, since no characteristic bands were observed in the O 1 s spectrum (Fig. S2).

Insight into the nibbling process

The temperature-programmed reduction technique (TPR) was used to gain insight into the etching of g-C₃N₄. The classic TPR-H₂ technique was used to observe hydrogen consumption with the thermal conductivity detector (TPR-TCD) as well as the TPR technique coupled with mass spectrometry (TPR-MS) and infrared spectroscopy (TPR-IR).

The TPR-MS and TPR-IR techniques allowed for identification of products formed during the etching of g-C₃N₄. During the TPR measurements, the gaseous products of the etching of g-C₃N₄ were monitored using a mass spectrometer in the range m/z = 1–53 (Fig. 4).

In the gaseous products of the reduction, ions with m/z = 12, 13, 14, 15, 16 generating from methane fragmentation were observed [34, 75]; ions with m/z = 14, 15, 16, 17 derived from ammonia [35, 75], and ions with m/z = 26, 27, 28 indicating the presence of hydrogen cyanide [75]. Moreover, signals from hydrogen and argon were recorded (from the reducing mixture) as well as small amounts of water and traces of air from the surroundings. The presence of CH₄, NH₃ and HCN in the etching products of g-C₃N₄ was confirmed by infrared spectroscopy (TPR-IR). Carbon nitride etching products were directed from the TPR apparatus to a gas cuvette placed in the IR spectrometer. Bands of CH₄, NH₃ and HCN were identified in the carbon nitride etching products on the basis of the reference spectra available at The National Institute of Standards and Technology (NIST) [33]. The changes that take place in g-C₃N₄ during reduction were observed by monitoring of the released gases using infrared spectroscopy (Fig. 5a, b) while the hydrogen consumption was monitored by a thermal conductivity detector (TPR-TCD)—Fig. 5. Nibbling of pristine gCN starts at *570°C* and proceeds with the highest speed at *710°C*—Fig. 5b1, c1. The presence of metal on the gCN surface significantly lowers the temperature at which carbon nitride etching begins. The temperature at which etching starts, increases in the following order: Ru/gCN(300°C) < Pt/gCN(400°C) < gCN(570°C)
The observed differences in reduction temperatures reflect different reactivities of both metals in hydrogenation of the C–N bonds. Ruthenium is known for its high activity in hydrogenolysis reaction of the C–N bond, higher than for platinum [53]; hence, the reaction is initiated at the lowest temperature (300 °C). Considering hydrogen consumption from the TPR-TCD plots (Fig. 5c), apparent activation energies (E_a [kJ mol⁻¹]) were calculated (Fig. S3) and they are:

\[
g_{\text{CN}}(E_a = 233) > \text{Pt/gCN}(E_a = 151) > \text{Ru/gCN}(E_a = 112; 155)
\]

The reduction/etching of gCN and Pt/gCN occurs as one step (one reduction peak); on the TPR-TCD plot for Ru/gCN there are two well separated signals (Fig. 5b3, c3)—E_a was calculated for each of them. The obtained activation energies for Pt/gCN and Ru/gCN are close to E_a of hydrogenation of amorphous carbon by Pt (140.1 ± 16.7 kJ mol⁻¹) and at the same time lower than for graphite supported platinum (181.9 ± 16.7 kJ mol⁻¹) [76].

The quantitative measurements of the gases released during etching of g-C₃N₄ are presented in Fig. 5b showing the results of TPR-IR investigations. Etching of pristine g-C₃N₄ is accompanied mainly by the emission of hydrogen cyanide and ammonia (Fig. 5a1, b1). The molar ratio of HCN:NH₃ is close to 3:1, which indicates that hydrogenation of g-C₃N₄ can take place according to the following reaction equation:

\[
\text{C}_3\text{N}_4 + 3\text{H}_2 \rightarrow 3\text{HCN} + \text{1NH}_3
\]

\[
\Delta H_{298}^\circ = -68 \text{ kJ mol}^{-1}
\]

\[
\Delta G_{298}^\circ = -152 \text{ kJ mol}^{-1}
\]  

Although the value of \(\Delta H^\circ\) is quite low, the reaction is exothermic. At the same time, the negative value of \(\Delta G^\circ\) indicates that the reaction is spontaneous.

Contrary to pristine g-C₃N₄, in the presence of metals the first etching products are ammonia and methane (Fig. 5a2, b2, a3, b3). For both the platinum and ruthenium catalysts, the molar ratio of NH₃:CH₄ is close to one. This means that the reaction can occur according to the equation:

\[
\text{C}_3\text{N}_4 + 12\text{H}_2 \rightarrow 4\text{NH}_3 + 3\text{CH}_4
\]

\[
\Delta H_{298}^\circ = -818 \text{ kJ mol}^{-1}
\]

\[
\Delta G_{298}^\circ = -709 \text{ kJ mol}^{-1}
\]

Reaction (2) is strongly exothermic and spontaneous. We believe that this reaction is the most important one during the etching of g-C₃N₄ in the presence of metals.

At higher temperatures, hydrogen cyanide appears in reaction products, and molar ratios for HCN:NH₃:CH₄ are approximately 1:3:2 (for Pt and Ru catalysts), which implies that etching of g-C₃N₄ can be described by the following reaction:
\[ \text{C}_3\text{N}_4 + 9\text{H}_2 \rightarrow \text{1HCN} + 3\text{NH}_3 + 2\text{CH}_4 \]
\[ \Delta H_{298}^o = -568 \text{ kJ mol}^{-1} \]
\[ \Delta G_{298}^o = -523 \text{ kJ mol}^{-1} \] (3)

for which \( \Delta H^o \) i \( \Delta G^o \) are also very negative.

Etching of g-C\(_3\)N\(_4\) in the presence of ruthenium occurs in two steps (contrary to gCN and Pt/gCN, which is a one-step process). In the first stage, the reaction products are only NH\(_3\) and CH\(_4\) appearing in equal amounts (Fig. 5a3, b3), which indicates the course of the reaction (2). In the second stage of etching (at higher temperature), the main products are HCN and NH\(_3\) (and small amounts of CH\(_4\)) implying that reaction (1) and/or (4) takes place:

\[ \text{C}_3\text{N}_4 + 6\text{H}_2 \rightarrow 2\text{HCN} + 2\text{NH}_3 + 1\text{CH}_4 \]
\[ \Delta H_{298}^o = -318 \text{ kJ mol}^{-1} \]
\[ \Delta G_{298}^o = -337 \text{ kJ mol}^{-1} \] (4)

In fact, the etching reactions (hydrogenation/hydrogenolysis) of g-C\(_3\)N\(_4\) can occur according to each of the above Eqs. (1–4) and their participation will be varied depending on the intrinsic activity of metals. The values of \( \Delta H^o \) and \( \Delta G^o \) are provided only for...
determining the probability of a specific reaction that can take place during the degradation of g-C₃N₄.

**Theoretical considerations and g-C₃N₄ etching mechanism**

In the structure of g-C₃N₄ nitrogen can be bonded to carbon through four different ways (Fig. 6):

| Bond          | Description                  | Energy (eV) |
|---------------|------------------------------|-------------|
| N–(C)₃        | Graphitic (quaternary nitrogen) | 3.3         |
| NH–(C)₂       | Imino-nitrogen               | 3.9         |
| –NH₂          | Amino-nitrogen               | 4.2         |
| –N=C–         | Pyridinic nitrogen           | 0.2 + 4.2   |

These bonds have different strengths, which have been estimated by calculations carried out in Gaussian16W [42] using the Hartree–Fock (HF) method and a basis set 6-311G(d). The results of the calculations are presented above in electron-volts. The series of chemical bond strengths was put in order according to the susceptibility of breaking the chemical bond. Thus, following the order of chemical bond strengths, one can propose the mechanism presented in Fig. 6. In the first step of g-C₃N₄ reduction, the bond (1) is broken, since its strength has the value of 3.3 eV. The next bond likely to be broken is bond (2) Fig. 6. Then, elimination of amino groups takes place (3), and almost at the same time hydrogenation of pyridinic nitrogen in the heptazine ring occurs (4) along with further hydrogenolysis of the single C–N bond (4′), which causes the opening of the aromatic ring in heptazine. This step seems to
be the key step for the subsequent stages of g-C₃N₄ destruction. It is highly probable that in the next steps, the amine group or methylamine can be eliminated, which undergoes further decomposition leading to ammonia and methane (4°). Once the aromatic ring of heptazine opens up, methane may be eliminated easily too (5). The direct elimination of HCN is also possible under higher temperatures (6). The sequence of chemical reactions shown above is consistent with the dynamics of releasing of ammonia, methane and hydrogen cyanide measured using the TPR-IR method described in the previous section.

It should be underlined at this point that the proposed mechanism of the g-C₃N₄ decomposition was based on estimations only. These estimations were obtained from bond energy calculations of particular bonds, taking into account simple theoretical model mentioned above (HF method and 6-311G(d) basis set). Moreover, not all the factors that influence the stability of particular bonds in the presence of metal nanoparticles were considered in the calculations, i.e., activation energy of reaction. The aim of our calculations was to put in order the strength of particular bonds according to their susceptibility to breaking and to propose the conceptual mechanism of hydrogenation/hydrogenolysis of graphitic carbon nitride that leads to the formation of sgCN.

**Conclusion**

On the basis of the obtained results one can present the structure of graphitic carbon nitride that undergoes the hydrogen reduction process at higher temperature and suggest the sequence of transformations that lead to formation of “spongy graphitic carbon nitride” (sgCN).

The structure of sgCN appears as a strongly defective graphitic carbon nitride. Metal nanoparticles (Pt, Ru) are the centers of hydrogen dissociation, which “attack” g-C₃N₄ causing the hydrogenation and hydrogenolysis of C–N bonds. The reactions take place on the surface of metal NPs, which are covered with oxidized forms of Pt and Ru capable of strong interactions with nitrogen, which was confirmed by XPS studies. Metal nanoparticles “move” through the structure of g-C₃N₄ like a “Pac-Man” etching the channels/tunnels in it, which produces a structure resembling a pumice stone with a well-developed specific surface area. So far, the phenomenon of channeling has been observed only for carbon materials [20–22, 24–29, 50, 54, 55, 77] as well as for boron nitride [56], but never for g-C₃N₄.

We do hope that the presented method of obtaining a high-surface area sgCN will inspire other scientists to attempt further modifications of g-C₃N₄. Selection of the right metal and the manner of its deposition on the g-C₃N₄ surface, its content as well as the adjustment of appropriate reduction conditions, create a wide range of possibilities to control over the structure of the resulting sgCN.

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**Author contribution**

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript. Conceptualization was contributed by MP, EA; writing—original draft, was contributed by MP, EA, IG; writing—review and editing, was contributed by MP, EA, MZ, IG, ZP; investigation was contributed by EA, MP, MZ, ZP, AS; methodology was contributed by MP, EA, IG; IG contributed to software; supervision was contributed by MP; visualization was contributed by MP, EA.

**Declarations**

**Conflict of interest** The authors declare no competing interests.

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