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N-Containing Graphene Preparation Using Melamine as a Nitrogen Source

N-doped graphene is not only a promising metal-free catalyst, but also a convenient carrier of metal nanoparticles for the creation of effective catalysts. Graphitic carbon nitride (g-C_3N_4) is used more often in photocatalytic processes and less often as electrocatalysts. This paper describes the preparation of N-containing carbon composites consisting of reduced graphene oxide (rGO) and g-C_3N_4 for the further creation of metal-carbon catalytic systems. These composites were prepared by the heat treating dry mixtures of graphene oxide (GO) and melamine (MA) in the temperature range of 450–550 °C in air. Oxygen-containing groups were identified in the graphene oxide samples synthesized by the modified Hummers method and in its reduced form. The thermogravimetric analysis method was used to determine the ranges of relative thermal stability of the GO + MA mixtures, which were found to be almost identical for the studied compositions with different component ratios. The structure of the graphene oxide and its composites with MA after heat treatment was studied by scanning electron spectroscopy, X-ray diffraction analysis, FTIR spectroscopy and elemental analysis. The effect of the ratio of the initial components on the formation of the heat treatment products was determined. It was shown that to obtain the rGO+g-C_3N_4 composites with a high content of carbon nitride, the ratio of the initial reagents should be taken equal to 1:2, and the heat treatment should be carried out at 550 °C.

Keywords: graphene oxide, oxygen-containing functional groups, melamine, "dry" preparation method, heat treatment, reduced graphene oxide, graphitic carbon nitride, elemental content

Introduction

The incorporation of nitrogen atoms into the structure of the carbon materials diversifies and improves their properties compared to their unmodified analogs. This is excellently confirmed by studies on the use of N-doped graphene as electrocatalysts in the oxygen reduction reaction [1–3]. There are many papers in the literature describing various methods for the synthesis of N-doped graphene, including chemical vapor deposition, thermal annealing, pyrolysis, arc-discharge, plasma treatment, hydrothermal and solvothermal methods, wet chemical synthesis, microwave treatment, and others [4]. The most popular and more accessible method for N-doping of graphene is the thermal treatment of graphene oxide (GO) in the presence of a nitrogen source, which can be ammonia, polyaniline, melamine, urea, polypyrrole or other nitrogen-containing substances. The most common N-precursor used to dope graphene is melamine, in which has at nitrogen content of 66.7 % by weight. For example, by carrying out ultrasonic treatment (UST) and prolonged stirring of a GO suspension in an aqueous solution of melamine, drying and heat treatment at 900 °C in a vacuum, N-doped graphene was prepared with a large surface area and a high percentage of pyridinic and graphitic N sites has been prepared, which determines its effective use in the electrocatalytic reduction of oxygen [5].

Most often, the heat treatment of GO with melamine mixtures is carried out in an inert atmosphere to prevent their rapid oxidation. Therefore, the authors of [6] performed the pyrolysis of GO + melamine samples, prepared from their suspension, at temperatures of 700–1000 °C in an argon environment to produce N-doped graphene. The dry mixtures of GO and melamine were also subjected to heat treatment at 800 °C in an argon atmosphere to form N-G samples, in which the atomic nitrogen content reached 10.1 % [7]. At the same time, in [8], based on thermogravimetric analysis (TGA), it was shown that the mass loss of the GO/melamine mixture when heated in a nitrogen environment and in air is almost the same, and the composition of the TGA products, according to X-ray photoelectron spectroscopy analysis, is the same. It was assumed that melamine can effectively prevent GO oxidation in air.

Due to the presence of various functional groups on the surface and the possibility of their further modification, high surface area, excellent transport, optical properties, and a number of other properties, N-doped graphene finds its application in the purification of wastewater from heavy metal ions, dye molecules and drugs, in the preparation of electrodes for electrochemical capacitors, fuel cells, as well as electrocatalysts, photocatalysts, catalysts and their carriers, in medicine and other fields of science and technology [4, 9–11].

In this paper, the investigations were conducted to prepare N-containing graphene, mainly consisting of reduced graphene oxide and graphitic carbon nitride (rGO + g-C_3N_4), for the further creation of catalysts from metal nanoparticles deposited on the N-modified graphene support. Melamine (MA) was used as a nitrogen source. The mechanically prepared GO+MA mixtures with different ratios of their components were heat-treated in the temperature range of 450–550 °C in closed crucibles in the air atmosphere of a muffle furnace. A detailed study of the structure, phase constitution and morphological characteristics of the products obtained after the thermal treatment was carried out.

Experimental

Materials

In the studies, graphite with a carbon content of ~99 % and particle sizes of 0–50 μm was used as the initial material for the preparation of the chemically modified forms of graphene. The chemical reagents, such as sulfuric acid H_2SO_4, potassium permanganate $KMnO_4$, hydrochloric acid HCl, and hydrogen peroxide were purchased from “Karagandareactivsbyt” LLP (Karaganda, Kazakhstan). Melamine was purchased from Sigma-Aldrich. Distilled water was used to prepare the required solutions and to wash the prepared carbon samples.

Oxide Graphene Preparation

The oxidation of the graphite was carried out using one of the modified Hummers methods [12]. In a typical synthesis, 100 ml of concentrated sulfuric acid were added to 4 g of graphite. The reaction mixture was stirred for 4 h at room temperature. Then, 12 g of potassium permanganate was added in portions, maintaining the temperature of the mixture below 10 °C. The resulting mixture was stirred for 8 h. As a result, a thick dark brown suspension was formed. Then, 200 ml of distilled water with 20 ml of a 30 % hydrogen peroxide solution were slowly added dropwise. Stirring was continued for another 30 min. The resulting suspension was filtered, and washed with 200 ml of 5 % hydrochloric acid solution and 1000 ml of distilled water to pH 7. The precipitate was dried at 50 °C. As a result, a loose black GO powder weighing 5.5 g was produced.

In order to study the change in the degree of functionalization of graphene oxide prepared by this method, the GO sample was sonicated at a power of 900 W for 1 h.

The presence of oxygen-containing functional groups (hydroxyl, carboxyl and epoxy) and their amount in the synthesized graphene oxide samples were determined by acid-base titration using the Boehm method, which is based on the fact that groups of different types have different acidities and can be neutralized by bases of different strengths [13, 14].

Preparation of the GO + MA mixed compositions and their heat treatment

Samples of mixtures from the synthesized graphene oxide and melamine (GO + MA) were prepared by a “dry” method, which consists of mixing GO and MA powders in mass ratios of 1:1, 1:2 and 1:5 and thoroughly grinding them in a mortar. The resulting dry mixtures of a certain mass were placed in crucibles with closed lids and heat-treated in a muffle furnace at 450, 500 and 550 °C for 3 h.

Characterization

IR spectra were recorded on an FSM 1201 Infrared Fourier spectrometer (LLC "Infraspek", Russia) for the initial graphite, the prepared graphene oxide samples with and without heat treatment (HT), as well as the heat-treated GO + MA mixtures. Their phase compositions were determined using a D8 ADVANCE ECO diffractometer (Bruker, Germany) in CuKα radiation in the angle range (2θ) 5–90°. The morphological features of the oxide graphene and its mixtures with MA were studied on a TESCAN MIRA 3 (Czech Republic) scanning electron microscope (SEM). Elemental microanalysis of the samples was performed using an X-Act energy dispersive detector (Oxford Instruments), and an Elemental Analyser EA3100 (EuroVector, Italy).

Results and Discussion

The content of oxygen-containing functional groups in the initial graphite and in the graphene oxide samples synthesized three times using the same route was determined by acid-base titration according to the Boehm method [13, 14]. All the obtained GO samples contained the three types of tested functional groups in approximately equal amounts in all three samples (Table 1). Ultrasonic treatment of GO for 1 h resulted in a slight decrease in the total amount of oxygen-containing groups, but the content of hydroxyl groups significantly decreased, while that of carboxyl and epoxy groups, on the contrary, increased. In the reduced graphene oxide prepared by chemical reduction using hydrazine hydrate, hydroxyl and carboxyl groups are absent and the epoxy groups remain in small amounts. In the thermally reduced graphene oxide, all detectable oxygen-containing groups were present, but the amount of epoxy groups increased significantly (Table 1). Partial preservation of the oxygen-containing groups in the reduced graphene samples was also observed in previous studies [15–17]. Surprisingly, the original graphite was also found to contain a small amount of epoxy groups (Table 1).

Table 1

Content of the functional groups in the original graphite and in the synthesized GO and rGO samples

GO samples	Sample weight, g	Total number of groups, mmol/g	Number of hydroxyl groups, mmol/g	Number of carboxyl groups, mmol/g	Number of epoxy groups, mmol/g
G	0.50	0.38	–	–	0.38
GO-1	0.50	5.02	1.54	2.80	0.68
GO-1 + UST	0.50	4.94	0.48	3.18	1.28
GO-2	0.20	5.05	1.56	2.85	0.64
GO-3	0.20	5.00	1.62	2.78	0.60
rGO-1, chem. red.	0.50	0.36	–	–	0.36
rGO, 450°C, 2 h	0.05	3.90	0.60	0.87	2.43

The presence of oxygen-containing groups in the graphene oxide was confirmed by the IR spectra obtained for one of its samples (Figure 1, spectrum *2*). The broad band in the region of 3450 cm^{-1} is attributed to the hydroxyl group, which indicates the presence of adsorbed water in this sample. The band at 1728 cm^{-1} is related to the deformation vibrations of the C=O bond in the carboxyl or carbonyl groups. The peaks at 1624, 1385, 1227 and 1061 cm^{-1} can be attributed to the stretching vibrations of the C=C, C–OH, C–O–C and C–O bonds. These results are in good agreement with the descriptions of the IR spectra of graphene oxide in previous studies [15, 18, 19]. Most of these peaks are absent in the structure of the graphite and thermally reduced graphene oxide (Figure 1, spectra *1* and *3*).

X-ray diffraction (XRD) analyses were performed for the initial graphite, graphene oxide and chemically reduced graphene oxide. The XRD pattern of graphite (Figure 2) shows a clear diffraction peak at 26.4° with the (002) phase, corresponding to the hexagonal arrangement of atomic layers with an interplanar distance of d = 3.37 Å, in agreement with the literature data [15].

In the XRD pattern of graphene oxide GO, the peak for the (002) phase is shifted to the region of smaller angles (2θ = 12.5°) due to an increase in the interplanar distance (7.08 Å) during the oxidation of graphite. This confirms the presence of oxygen-containing functional groups in the GO structure. In the reduced graphene oxide rGO, the interplanar distance decreases again without preserving the crystal structure due to the loss of some of the functional groups. Its XRD pattern shows a broad peak for the (002) phase with a slight shift towards smaller angles (2θ = ~24.5°) (Figure 2). The particle sizes of the graphene in this phase, calculated using the Debye-Scherrer method within the diffractometer software, are ~17 nm. There is also a low and broadened peak for the (101) phase in the angle range 2θ = ~43–44°.

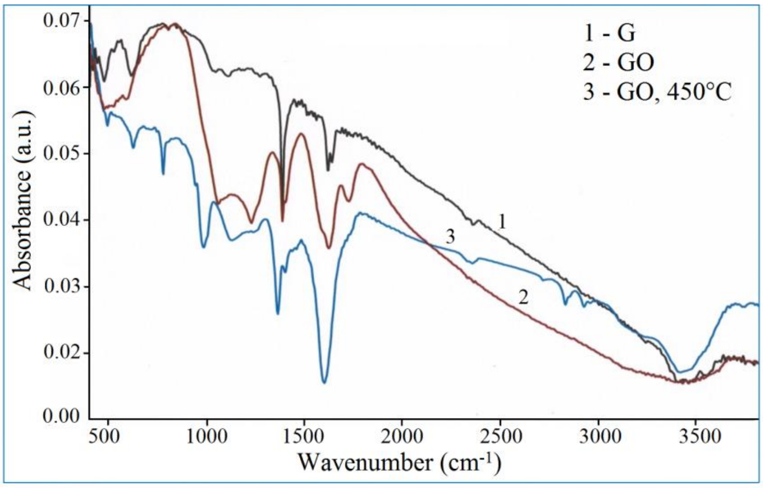

Figure 1. IR spectra of graphite (*1*), graphene oxide (*2*), and graphene oxide heated at 450 °C (*3*)

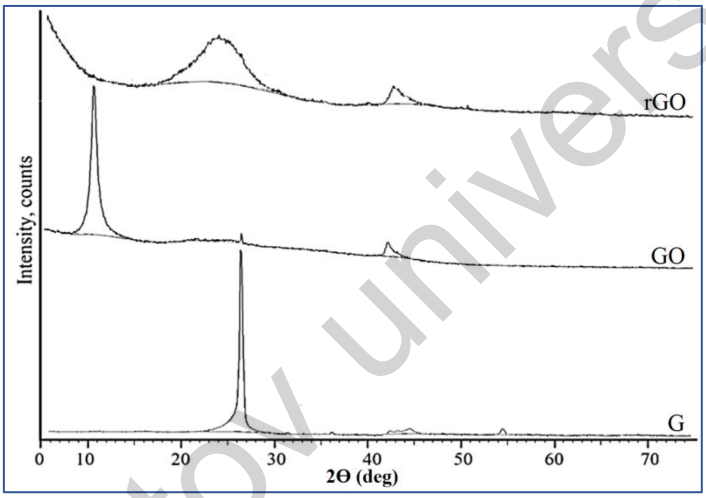

Figure 2. XRD patterns of graphite G, graphene oxide GO and chemically reduced graphene oxide rGO

The morphology of the synthesized graphene oxide has been studied using an electron microscope; its micrographs are shown in Figure 3. As known from the literature, the implantation of functional groups overcomes the van der Waals sheets and increases the distance between the layers, i.e., graphite exfoliation occurs (Figure 3, *a* and *b*). The delaminated layers in synthesized graphene oxide have different thicknesses: ~50–180 nm. When this sample is exposed to ultrasound, its structure changes and becomes curly with thin and light layers (Figure 3, *d*), but denser layers also remain (Figure 3, *c*). According to the energy-dispersive spectroscopy (EDS) analysis, GO contains elements such as carbon (~74 %), oxygen (~24 %) and small amounts of sulfur (due to the use of sulfuric acid in the syntheses). After ultrasound treatment, the oxygen content in GO decreased to 17 %, and the carbon content increased to 81 %, indicating a decrease in the oxygen-containing groups in this sample and confirming the data in Table 1.

To improve the interaction of the metal catalyst particles with the carbon carrier and to enhance the electron transport, N-doping of the graphene carbon layers have been N-doped using various methods. Most often, such modification of graphene is carried out at high temperatures (800–1000 °C) and in an inert atmosphere, which is economically and technically quite expensive. Therefore, attempts are constantly being made to simplify these methods. For example, in paper [8], the possibility of simultaneous reduction and N-doping of graphene in an air environment at a temperature of 430 °C was established and NrGO samples with high catalytic activity in the oxygen reduction reaction were prepared.

In this work, to create N-containing samples of thermally reduced graphene oxide and subsequently produce catalytic systems based on them, melamine was chosen as a nitrogen source that is a chemical compound well enriched with nitrogen and therefore often used to create N-doped carbon materials.

The GO + MA mixtures were prepared using the method of mechanical mixing of graphene oxide and melamine powders with ratios of 1:1, 1:2 and 1:5, and thermogravimetric studies of the thermal stability of these mixtures and their individual components were carried out (Figure 4).

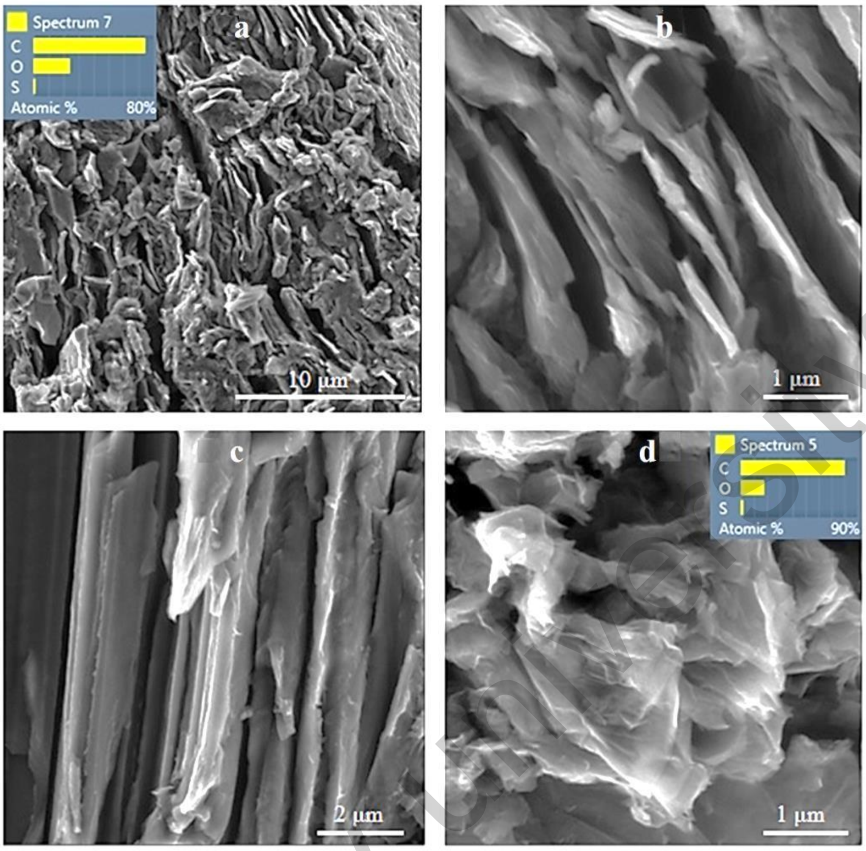

Figure 3. SEM images of synthesized GO (*a*, *b*) and GO+UST (*c*, *d*)

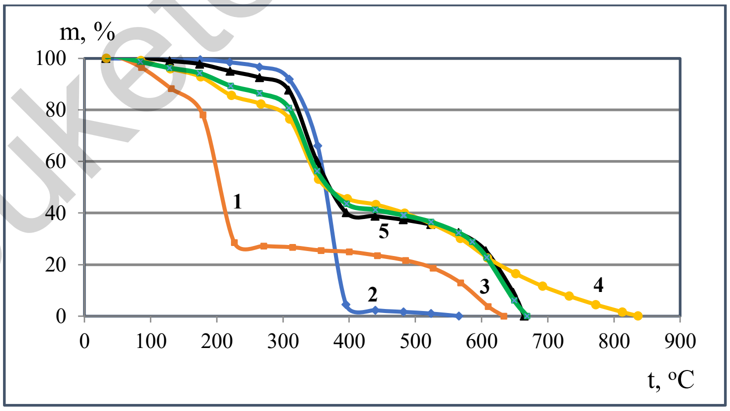

Figure 4. TGA curves for graphene oxide (*1*), melamine (*2*) and their mixtures with ratios (1:1) (*3*), (1:2) (*4*), and (1:5) (*5*)

According to the TGA data, the thermal decomposition of graphene oxide occurs in four temperature ranges with different mass losses (Figure 4, curve 1). The first is in the range of 70–180 °C with a mass loss of ~22 %, mainly due to the evaporation of the adsorbed water. In the second temperature range (~180–203 °C), a strong loss of the GO mass is observed (up to 70 % of the initial one), apparently due to the decomposition of the oxygen-containing groups. The third region (205–495 °C) is relatively stable, with a mass loss of only 10 %. In addition, the fourth region is ~500–630 °C, where the final combustion of carbon residues interacting with oxygen occurs.

Melamine is thermally stable up to almost 300 °C with a mass loss of only 6 % (Figure 4, curve 2). However, during the next 100 °C (up to 400 °C), it decomposes abruptly and completely. Mixtures of GO with melamine behave differently (Figure 4, curves 3–5). When heated to approximately 300 °C, all three GO + MA samples with different component ratios lose from 20 % (1:2 mixture) to 10 % (1:5 mixture) in mass, apparently due to changes in graphene oxide. Then, there is a sharp mass loss (by a further ~ 30 %) up to 400 °C, after which relatively horizontal sections (in the 400–550 °C range) with small mass losses appear on the TGA curves. This is followed their final combustion occurs. As suggested in [8], the presence of melamine in a mixture with graphene oxide prevents its rapid oxidation. The gases released during the decomposition of melamine, and primarily ammonia, create an atmosphere that protects graphene oxide from rapid decomposition in the air and simultaneously have an N-doping effect on graphene.

It is known from the literature [20–22] that melamine (as well as cyanamide, dicyanamide, etc.) undergoes condensation during thermal treatment in an inert atmosphere, first with the formation of melam, melem, then melon, and finally a polymer product is formed — graphitic carbon nitride, g-C_3N_4 (Figure 5), which is one of the allotropic formations of the polymer with the general formula $(C_3N_3H)_n$. It consists of tri-S-triazine rings linked by amino groups (Figure 5). This gives it high thermal stability (600 °C in air) and chemical resistance in both acidic and alkaline environments.

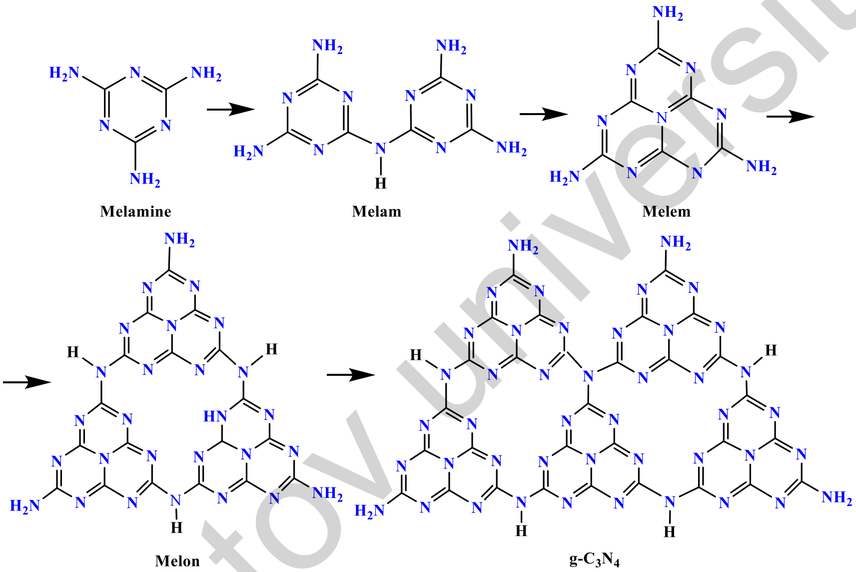

Figure 5. Scheme of the thermal transformation of melamine

In order to produce the samples of reduced graphene containing nitrogen, the mechanical mixtures of GO + MA with mass ratios of 1:1 and 1:2 were subjected to heat treatment (HT). The HT temperature was selected based on the TGA data from the region in which these mixtures retained stable, i.e. 450–550 °C (Figure 4). The powders of both components which had been ground in a mortar were placed in crucibles with closed lids and processed in a muffle furnace at the given temperature for 3 hours.

The IR spectrum of the thermal condensation products of melamine treated at 450 °C (Figure 6, *a*, spectrum 1), shows the characteristic vibrations of triazine cycles are present in the region from 1640 cm^{-1} to 1240 cm^{-1} [21]. The spectra of melamine after HT at 500 and 550 °C are similar and differ significantly from the spectrum of melamine with HT at 450 °C. These spectra show intense bands at 1616 cm^{-1} and 1470 cm^{-1}, which are related to the intermediate condensation products melem and melon (Figure 6, *a*). The first of these bands is also present in the spectrum of the GO + MA (1:1) mixture after heat treatment at 450 °C (Figure 6, *b*, spectrum 1) and overlaps with the band for the stretching vibration of the C=C bond in the benzene rings of graphene and/or for the vibration of the C=N bond in the triazine rings. The absorption bands in the region of 3100–3500 cm^{-1} in the spectra of the thermally treated melamine (Figure 6, *a*) and in the region of 3400–3550 cm^{-1} in the spectra of the GO + MA (1:1) mixture after HT (Figure 6, *b*) indicate the presence of $-NH_2$ and =NH groups in the resulting products, which indicates the incomplete condensation of the intermediate products and the formation of the g-C_3N_4 polymer product even at a temperature of 550 °C. The bands at 1362 and 1400 cm^{-1} in the spectrum of the GO + MA (1:1) mixture after heating at 500 and 550 °C may belong to the C–N bond vibrations in the carbon nitride [23].

XRD analyses were performed for the products resulting from the heat treatment of melamine and its mixtures with graphene oxide at ratios 1:1 and 1:2 (Figure 7). These analyses revealed changes in phase constitutions as the heat treatment temperature increased. This is particularly evident in the XRD patterns of both the melamine itself and the GO + MA mixtures with a change in temperature from 450 to 500 °C. The XRD pattern of melamine treated at 450 °C is represented by a set of diffraction peaks that coincide well with the XRD pattern of the intermediate compound melem (2,5,8-triamino-tri-s-triazine) [24] (its structure is shown in Figure 5).

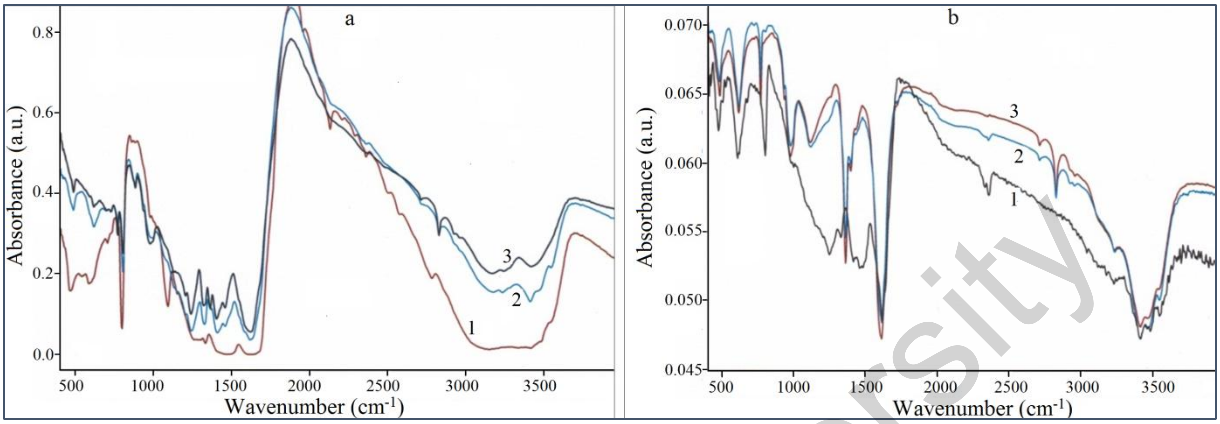

Figure 6. IR spectra of melamine (*a*) and GO + MA (1:1) mixtures (*b*) treated at 450 °C (*1*), 500 °C (*2*) and 550 °C (*3*)

The X-ray diffraction patterns for both GO + MA mixtures conditioned at the same temperature have flattened peaks at the same angles with a noticeably weaker intensity (Figure 7, *a*). When melamine is treated at 500 °C (Figure 7, *b*), the products formed consist mainly of graphitic carbon nitride, g-C_3N_4 (the main peaks in its standard XRD pattern are located at the angles of 27.46° and 12.93°). There are also insignificant impurities apparently of incompletely reacted melem or melon. According to the XRD pattern in Figure 7, *c*, the treatment of melamine at 550 °C also leads to the formation of g-C_3N_4.

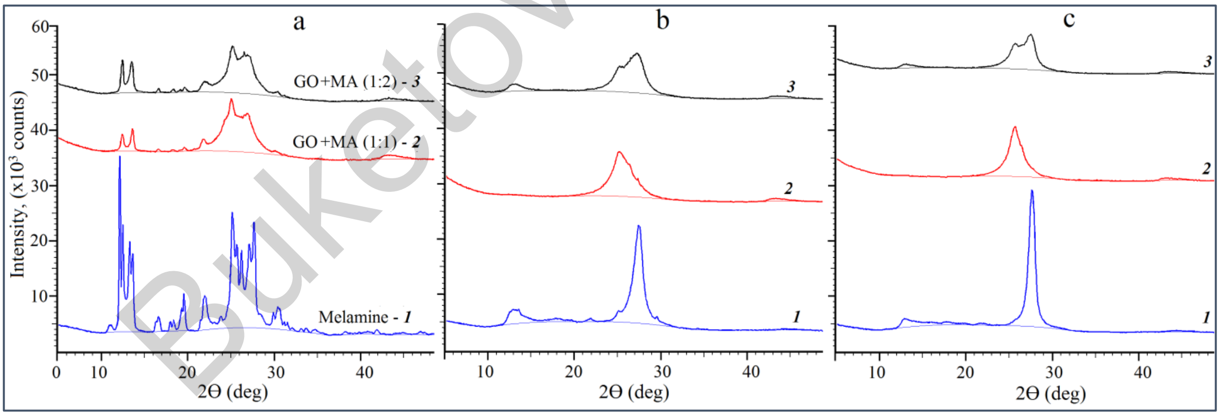

Figure 7. XRD patterns of melamine and its mixtures with graphene oxide after heat treatment at 450 °C (*a*), 500 °C (*b*) and 550 °C (*c*)

The XRD patterns of the GO + MA (1:1) mixture after HT at 500 and 550 °C are represented by one broad peak with a maximum at $2\theta = 25.5°$, which corresponds to the (002) phase of the reduced graphene oxide ($2\theta = 24.5°$, Figure 2), but with a slight shift in the diffraction angle. This peak also covers the peak at $2\theta = 27.37°$, which belongs to the graphitic carbon nitride. The same peaks, but with greater intensity for g-C_3N_4, are also clearly visible in the XRD patterns of the GO + MA mixture with an increased melamine content (the ratio of the initial components was 1:2) which was thermally treated at 550 °C (Figure 7, *b* and *c*). It can therefore be concluded that during the heat treatment of the mechanically prepared mixtures of GO and melamine in the temperature range of 500–550 °C, two crystalline phases were formed: reduced graphene oxide and graphitic carbon nitride. As in previous studies [8], it is assumed that, the partial introduction of nitrogen atoms into the graphene structure occurs under the action of released ammonia, resulting in the formation of N-doped reduced graphene oxide, which is most often obtained at higher temperatures and in an inert environment.

Microscopic studies of the GO + MA (1:1) mixture after heat treatment showed that in the products formed both at 450 °C and at 500 °C, the graphene layers are separated (Figure 8), and their thickness ranges from 7 to 45 nm. That is, as a result of heat treatment, multilayer graphene is formed, covered with adsorbed products of the heat-treated melamine, including g-C_3N_4.

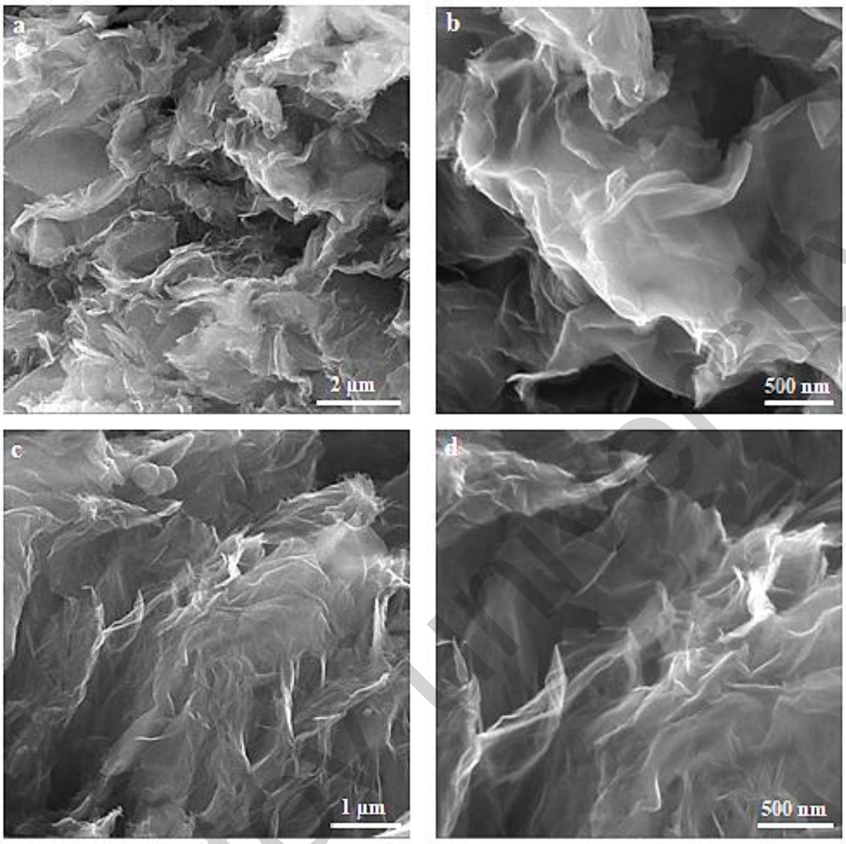

Figure 8. SEM images of the GO + MA (1:1) mixture after heat treatment at 450 °C (*a*, *b*) and 500 °C (*c*, *d*)

The distribution of chemical elements (C, N and O) over the surface of the rGO + g-C_3N_4 composite particles prepared by heat treatment of the GO + MA (1:2) mixture at 550 °C is shown in Figure 9. These EDS analyses were performed on a ZepTools ZEM20 microscope (China) using an Oxford AZtec instrument (UK). As can be seen from the images, nitrogen is distributed quite densely across the entire surface of this composite with some localization occurring in certain areas. This confirms the polymerization of intermediate compounds formed during the heat treatment of melamine and the formation of g-C_3N_4.

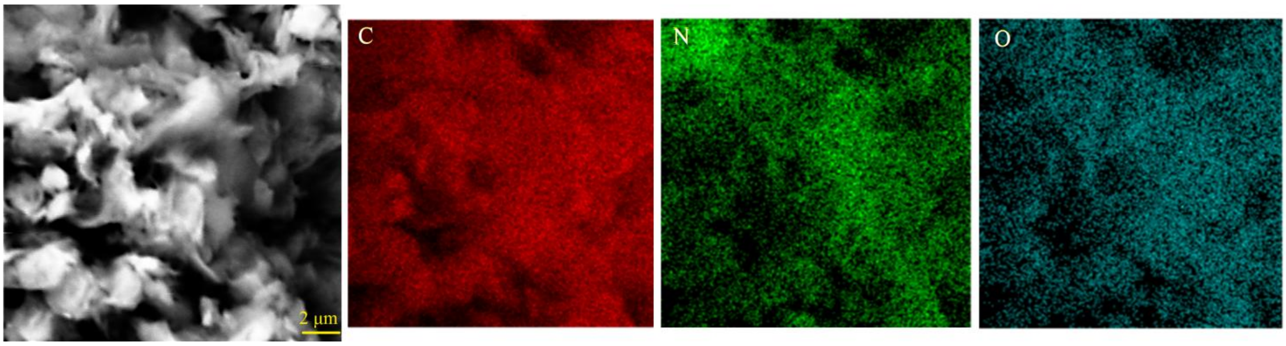

Figure 9. SEM images of the GO + MA (1:2) mixture after heat treatment at 550 °C
and distribution of chemical elements in the surface layer of its particles

An elemental analysis was carried out for the products formed after HT of the dry GO + MA mixtures (Table 2). This analysis revealed that the initial amount of melamine in the mixture with GO affects the way it transforms during the thermal treatment.

Table 2

The element contents (C, N, H) in melamine and GO + MA mixtures samples after their heat treatment

Samples	Temperature of HT, °C	Elements Content, %		
		C	N	H
MA	450	33.39	63.97	2.61
MA	500	34.56	63.05	1.89
MA	550	35.00	62.81	1.86
GO + MA (1:1)	450	57.80	33.82	1.68
GO + MA (1:1)	500	76.10	13.00	0.94
GO + MA (1:1)	550	82.18	6.76	–
GO + MA (1:2)	450	49.27	44.21	1.74
GO + MA (1:2)	500	52.44	41.54	1.49
GO + MA (1:2)	550	57.49	35.56	1.52

It follows from the data in Table 2 that the heat treatment of the GO + MA (1:1) mixture in the temperature range of 450–550 °C is accompanied by a sharp decrease in the nitrogen content, which indicates the predominant decomposition of melamine and the formation of a small amount of its condensation product g-C_3N_4. When treating a mixture with a large amount of melamine, i.e., GO + MA (1:2), the nitrogen content also decreased with increasing temperature, but not as significantly as in the case of a mixture with a ratio of 1:1 (Table 2). At the same time, after treating this mixture at 550 °C, graphitic carbon nitride was formed, which was confirmed by XRD analyses (Figure 7, *c*). For melamine itself, its heat treatment in the studied temperature range led to the formation of the g-C_3N_4 product (Figure 7, *c*), the decrease in nitrogen in this temperature range was minimal (Table 2), which is in good agreement with the results of the elemental analysis of melamine in [21]. The existence of hydrogen in the studied samples indicates their incomplete deamination and the presence of terminal –NH and –NH_2 groups.

Graphitic carbon nitride, being a polymer semiconductor with a unique electronic structure, is in great demand in various modifications as a photocatalyst for use in processes such as water splitting and organic photosynthesis [25, 26]. Intensive research is being carried out on the creation of metal/g-C_3N_4 composites to improve the semiconductor and photocatalytic properties of carbon nitride and expand the areas of its application [27]. Combining g-C_3N_4 with graphene increases the mechanical strength of their composites, promotes charge transfer and electron-hole separation, which can improve the electrical conductivity and electrocatalytic properties of g-C_3N_4/graphene composites, that has been demonstrated in important electrochemical reactions of oxygen reduction and the formation of hydrogen and oxygen [28]. The products of the heat treatment of the GO and melamine mixtures obtained by us, consisting of reduced graphene and graphitic carbon nitride, as well as partially of N-doped graphene with the incorporation of nitrogen atoms into the graphene structure, will be used as carriers for metal nanoparticles in the creation of catalysts for the electrocatalytic syntheses of organic compounds. It should be noted that the metal-carbon electrocatalysts prepared by us on the basis of pyrolyzed polymers (melamine-formaldehyde and aniline-formaldehyde), as well as carbon nanotubes, showed high electrocatalytic activity in the electrohydrogenation of organic compounds [29, 30].

Conclusions

The performed investigations have shown the possibility of producing N-containing carbon material consisting of reduced graphene oxide and graphitic carbon nitride (rGO + g-C_3N_4) by the heat treatment of mechanical mixtures of graphene oxide powders prepared by the modified Hummers method, and melamine as a nitrogen source. The effect of the ratio of these components on the formation of heat treatment products in an air environment has been established. It has been shown that the GO:MA ratio of 1:2 is more favourable for preparing the carbon base rGO + g-C_3N_4. The prepared samples of N-containing graphene will be used to create metal-carbon catalysts for using them in the electrocatalytic syntheses of organic compounds.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Nina Mikhailovna Ivanova** conceptualization, writing-original draft, methodology, validation, visualization, writing-review & editing; **Zainulla Muldakhmetovich Muldakhmetov** funding acquisition; **Yakha Amkhadovna Vissurkhanova** investigation, methodology, data curation, visualization; **Yelena Anatol'evna Soboleva** investigation, data curation, Figures design, resources, visualization; **Askhat Sakenovich Borsynbayev** conducting spectral analyses.

Conflicts of Interest

The authors declare no conflict of interest.

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