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SYNTHESIS OF MULTILAYER AZAGRAPHENE AND CARBON NITRIDE OXIDE

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As an one of the most promising materials of green energy as a photocatalyst for the production of hydrogen from renewable, natural sources (water, greenhouse gas) and environmental remediation through the degradation of toxic organic pollutants, graphite-like carbon nitride (characterized as a non-toxic and chemically highly resistant material) and its nanostructured and doped (especially by oxygen atoms) derivatives attract special attention. The actual task for expanding the scope of application of g-C_3N_4 is to improve and optimize its catalytic, electronic and optical properties by increasing both the surface area of graphitic carbon nitride and the number of active centers of the carbon nitride network due to doping of carbon nitride. The use of a mixture of two different precursors ensures the creation of heterojunctions, and as a result, an improvement the photocatalytic characteristics of g-C_3N_4. The oxygen-doped carbon nitride (O-g-C_3N_4) and water-soluble carbon nitride oxide (g-C_3N_4)O was simultaneously synthesized by the gas phase method under special reaction conditions of pyrolysis of cyanuric acid and urea mixture. Reduction by the hydroquinone of carbon nitride oxide (g-C_3N_4)O yields nanostructured reduced carbon nitride (or reduced multilayer azagraphene). Obtained products were characterized by using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), chemical and X-ray diffraction (XRD) analyses, scanning electron microscopy (SEM). According to the results of XPS and IR spectrometry the chemical bonds between atoms in a heteroatomic plane of reduced carbon nitride (RCN) correspond to the bonds in a synthesized carbon nitride (SCN). However, according to XRD results, reduced carbon nitride (RCN) probably consists of poorly connected heteroatomic azagraphene layers, because it has a significantly larger (on 0.09 nm) interplanar distance between the adjacent nitrogen-carbon layers than interplanar distance between the layers of synthesized carbon nitride (SCN). By SEM characterization it was found that the pyrolysis of a mixture of various precursors (cyanuric acid and urea) yielded a product with smaller crystalline domains (which can improve photocatalytic characteristics) than the pyrolysis of a single precursor (urea only).

Keywords: azagraphene, carbon nitride oxide, cyanuric acid, urea, pyrolysis, photocatalyst

INTRODUCTION

For the first time, a product similar in composition to C_3N_4 as a porous bulk amorphous mass was obtained as early as 1922 by decomposition of mercury thiocyanate $Hg(NCS)_2$ [1]. Though graphite-like carbon nitride is one of the oldest materials described in the chemical literature, only today, at the level of modern technology, g-C_3N_4 experiences a renaissance as a highly active photocatalyst which absorbs light in the visible range [2–5]. Given that this polymer, not containing metal, is capable to generate hydrogen in visible light (since it was first adopted as a metal-free polymeric semiconductor for photocatalytic water-splitting to produce hydrogen and oxygen in 2009 by Xinchen Wang and his co-workers [6]). Thus, the renewed interest of researchers in graphite-like carbon nitride occurred in the 21st

century primarily as one of the most promising materials of green energy as a catalyst for the production of hydrogen from renewable, natural sources (water, greenhouse gas) and environmental remediation through the degradation of organic pollutants and destruction of pathogenic microflora (viruses and bacteria) [2–5]. With intriguing features such as chemical and thermal stability, low cost, ease of preparation and visible light response, applications relevant to graphite-like carbon nitride as a semiconductor (with the band gap 2.7 eV, corresponding to an optical wavelength of 460 nm) prevails in photocatalytic, photoelectrochemical, photovoltaic, chemical sensing, fluorescent bioimaging and some other areas [4, 7–10].

In recent times, the object of increasing interest of researchers is the doped with atoms of other elements (in particular, oxygen) and

nanostructured g-C$_3$N$_4$ [2–5, 11–14]. The actual task for expanding the scope of application of g-C$_3$N$_4$ is to improve and optimize its catalytic, electronic and optical properties both by increasing the surface area of graphitic carbon nitride and by increasing the number of active centers of the carbon nitride network, due to an increase in the number of structure defects due to doping of carbon nitride. For example, nanosheets dispersed in an aqueous medium (6–12 two-dimensional heteroatomic monolayers 2–4 nm thick) obtained by ultrasonic peeling of powdered g-C$_3$N$_4$ in an acid medium have almost 6.4 times greater photocatalytic activity [15]. Carbon nitride nanosheets are distinguish by stronger photoluminescence, good biocompatibility and are more effective nonmetallic biosensors than bulk g-C$_3$N$_4$ [16, 17]. The doping of different non-metal elements (in particular, oxygen) can promote the delocalization of the π-conjugated electrons, which is fundamentally important for improving the conductivity, mobility and separation of photo-generated electrons, thus greatly enhancing the photocatalytic performances of doped g-C$_3$N$_4$ [5, 18–25]. It is assumed that the self-modulation of the electronic and band structure arises in the lattice of O-doped carbon nitride [18]. As a result, the O-C$_3$N$_4$ photoactivity boundary in the visible spectrum expands from 460 to 498 nm [18] or more (up to 700 nm [23]). Ozone treated carbon nitride (OCN) accelerates the photodegradation of methylene blue by a factor of 5 times and 2 times accelerates the generation of H$_2$ in comparison with untreated g-C$_3$N$_4$ [24]. Doping carbon nitride with oxygen (by oxygen-plasma treatment) according to the study [25] does not influence the structure of g-C$_3$N$_4$ but changes its morphology, increases the surface area, decreases the band gap energy and increases the separation efficiency of photogenerated electrons and holes, which increase photocatalytic RhB degradation constants by approximately 6 times. And in oxygen-doped g-C$_3$N$_4$ obtained by hydrothermal treatment of carbon nitride synthesized from a mixture of melamine and thiourea, for example, due to decomposition of the Acid Orange 7 dye (C$_{16}$H$_{11}$N$_2$NaO$_4$S), the photocatalytic response rate is 10 times higher, while the photocatalytic activity in 7 times higher than that of untreated g-C$_3$N$_4$ [19].

We emphasize that most known methods of functionalization of carbon nitride are multistage (at least two-stage) methods, since post-synthesis treatment of previously synthesized g-C$_3$N$_4$ is assumed [18–20, 24, 25]. The Kharlamov's laboratory firstly proposed a one-stage method for the direct synthesis of oxygen-doped carbon nitride [26, 27]. In addition, for the first time, a new substance – carbon nitride oxide (g-C$_3$N$_4$)O, was synthesized in our laboratory by the gas phase method under special reaction conditions of melamine [26] and urea [27] pyrolysis. Later, a group of European scientists synthesized carbon nitride oxide from urea under hard conditions at high pressure (3 GPa) in a diamond anvil [28]. However, we believe that the facile method developed by us for the production of carbon nitride oxide (g-C$_3$N$_4$)O by heat treatment at atmospheric pressure of low-cost and affordable precursors (melamine, urea or, as proposed in the present study, mixture of cyanuric acid and urea) is currently the most economical and efficient.

To synthesize N-graphene (azagraphene [29], in the monolayer of which the maximum possible number of carbon atoms is replaced by nitrogen atoms), from carbon nitride (as graphene was obtained from graphite) is the most interesting and topical task of the next stage of development of nanochemistry after successful synthesis of carbon monatomic molecules and nanostructures. In our laboratory, the first steps were taken to obtain an isostructural analog of graphene – azagraphene by a method analogous to the method of synthesis multilayer graphene by reduction of graphite oxide [29].

EXPERIMENTAL

The synthesis of carbon nitride oxide by thermal treatment of cyanuric acid and urea mixture (in 1 : 1 ratio) was carried out in accordance with the pyrolysis method described for the simultaneously production of oxygen-doped carbon nitride (O-g-C$_3$N$_4$) and carbon nitride oxide (g-C$_3$N$_4$)O from melamine [26] or urea [27]. The main feature of a special reaction conditions of pyrolysis is that the products are formed in an vapor-gas reactionary space and mainly are located by means of the deposition and the condensation in more lowly temperature (concerning the most highly temperature reaction zone) zones of reactionary space, far from a

place of precursor localization [26, 27, 30]. The retainable pyrolysis-generated self-supporting atmosphere is the necessary condition. Studies were conducted by varying the temperature, the amount of precursor (cyanuric acid and urea equimolar mixture) in the crucible and the duration of its heat treatment. The experiments were carried out under ambient pressure in the temperature range 450–600 °C. The precursor was localized in an open ceramic crucible placed in a tubular quartz reactor with one open end to exit a self-generated reactive vapor-gas mixture that bubbled through water. The rate of heating of a ceramic crucible with a precursor did not exceed 10 deg·min^{-1}.

The reduction of the synthesized (from cyanuric acid and urea mixture) samples of carbon nitride oxide (CNO) was carried out on a technique described for the reduction of graphite and graphene oxides by hydroquinone. Hydroquinone acts as a reducing agent by losing either one H^{+} from one of its hydroxyls to form a monophenolate ion or two H^{+} from both hydroxyls to form a diphenolate ion (quinone) and the reduction process must involve the removal of the oxygen functional groups of carbon nitride oxide. The carbon nitride oxide was dispersed in the water and the hydroquinone was added. The mixture was boiled for 20 h with magnetic stirring and final products were isolated by centrifugation, washed very well with water and acetone, and finally dried.

Synthesized samples of carbon nitride, carbon nitride oxide and the products of its reduction by hydroquinone were investigated by the methods of scanning electron microscopy (SEM), chemical and X-ray diffraction analyses as well as by the method of XPS and FT-IR spectroscopy. The FT-IR spectra in the reflectance mode were recorded in the range from 4 000 to 450 cm^{-1} with the spectral resolution of 8 cm^{-1} using a Nexus Nicolet FTIR spectrometer (Thermo Scientific) equipped with a Smart Collector reflectance accessory. Samples under investigation were powdered with KBr in 1 : 100 ratio. X-ray diffraction study of powders was fulfilled on DRON-UM diffractometer with CuK_{α}-radiation and nickel filter. X-ray photoelectron spectra of the samples were measured with photoelectron spectrometer manufactured by SPECS Surface Nano Analysis Company (Germany) with a PHOIBOS 150 hemispherical analyzer.

The content O, H, N in the products was determined by a method (developed by IPMS of National Academy of Sciences of Ukraine) of pulse heat treatment (~ 2500 °C) of the sample by the carbon. Subsequently the resulted products of reduction (CO, H$_2$, N$_2$) were chromatographically (a universal chromatograph LHN-80, Russia) separated in a flow of helium. The content of carbon in a sample after its oxidation up to CO$_2$ was determined by the express analyzer (an apparatus AN 7560M, Russia) with the coulometric titration cells of CO$_2$ in a flow of oxygen.

RESULTS AND DISCUSSION

At the heat treatment at 550 °C of a mixture of cyanuric acid and urea, two products are formed. The diffractogram of the first brown unsoluble powdered product A (Fig. 1, curve *1*) contains two intensive reflexes at $2\theta = 27.49$ and $12.40°$ as well as a weak reflex at $2\theta = 21.45°$ which characteristic for oxygen-doped graphite-like carbon nitride (O-g-C$_3$N$_4$) [26].
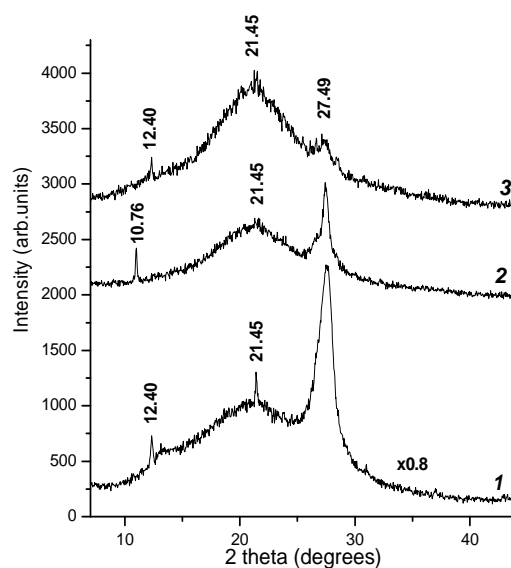

Fig. 1. X-ray diffraction spectra of: *1* – synthesized carbon nitride (product A), *2* – carbon nitride oxide (product B) and *3* – reduced carbon nitride (product C)

These two intensive reflexes, as known, are caused by an interlayer stacking of aromatic heteroatomic rings with an interplanar distance $d = 0.324$ nm, and the periodicity of stacking of heptazine fragments in one layer ($d = 0.714$ nm), respectively. According to the chemical analysis the first product A contains 5.7 mass. % of

oxygen, the ratio C/N is equal to 0.76 and is close to the stoichiometric ratio (0.75) for O-doped graphite-like carbon nitride (O-g-C_3N_4) [26].

The SEM characterization results revealed that the samples synthesized from different precursors have significantly different morphology. Specifically, it was found that the pyrolysis of mixture of different precursors (cyanuric acid and urea) yielded product with smaller crystalline domains (Fig. 2 *a*) compared to that of urea only ((Fig. 2 *b*). It is important to note that the polymeric nature of g-C_3N_4 facilitates the tuning of its band gap structure by simply using different precursors, variation of pyrolysis conditions and doping [31]. The reported band gap energies of g-C_3N_4 range from 2.4 to 2.8 eV dependent on the using different precursors [31]. The use of a mixture of two different precursors ensures the creation of heterojunctions, and as a result, an improvement the photocatalytic characteristics of g-C_3N_4 [31].
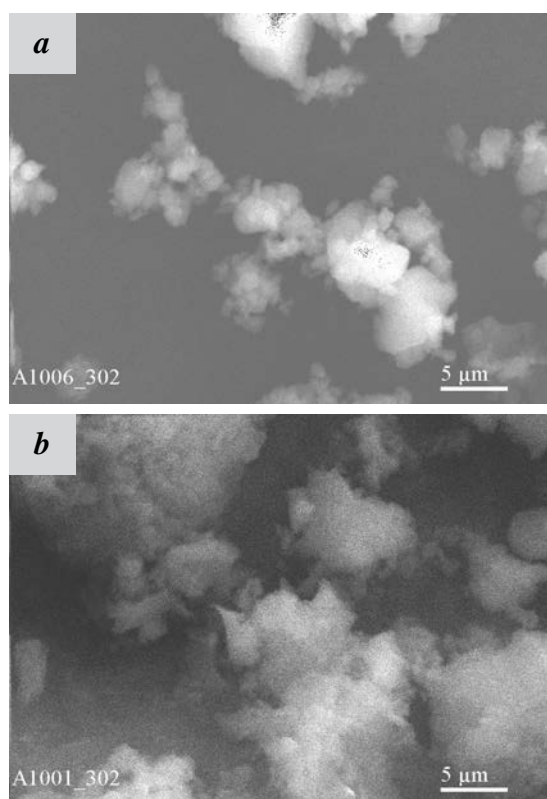
Fig. 2. SEM images of O-doped carbon nitride samples obtained from cyanuric acid and urea mixture (*a*) and from urea (*b*)

The second product B dissolves in boiling water to form a flocculent solution of yellow color. From a solution of the second product B after an evaporation of water a powder of dark yellow color is crystallized, on a diffractogram (Fig. 1, curve *2*) which three reflexes are visible at 2θ = 10.79, 21.45 and 27.49 °. Three reflexes at 2θ = 10.76 (*d* = 0.818 nm), 21.45 (*d* = 0.414 nm) and 27.49 ° (*d* = 0.324 nm), are characteristic for carbon nitride oxide (g-C_3N_4)O [14, 26–29].

The most intense reflex at 2θ = 27.49 ° (*d* = 0.324 nm), characterizing the interlayer distance in g-C_3N_4, is presented in the diffractogram of a carbon nitride oxide (product B) synthesized from cyanuric acid and urea mixture. The appearance of an additional reflex at 2θ = 21.45 ° (*d* = 0.414 nm) in the X-ray diffraction pattern of carbon nitride oxide is associated, as suggested in [26], with partial distortion of the planarity of its polymer network ((C_6N_7)–N)$_n$ due to the dearomatization of some heterocycles during oxidation (Fig. 3 *b*). With an increase in the number of oxygen-containing groups between adjacent planes, the peak 2θ = 21.45 ° transforms into a wide halo, but the reflex at 2θ = 27.49 ° also persists, since in carbon nitride oxide the oxygen-containing groups are predominantly localized in the voids of the «openwork» plane (Fig. 3 *b*). It is also noteworthy that the reflex at 12.40 ° (*d* = 0.714 nm), characterizing the distance between the heptazine fragments (C_6N_7) in the g-C_3N_4 plane of product A, is shifted to 10.76 ° (*d* = 0.818 nm) in the diffractogram of carbon nitride oxide (product B) synthesized from cyanuric acid and urea mixture. The increase in this distance in the heptazine monolayer (g-C_3N_4)O at 0.104 nm is due to the break of some C–N bonds between the heptazine moieties and the tertiary nitrogen atom in the dimers (C_6N_7)–N–(C_6N_7) [27].

According to the elemental chemical analysis, yellow carbon nitride oxide powder (synthesized from cyanuric acid and urea) contains 15.9 % oxygen. The C/N ratio in carbon nitride oxide sample (product B) obtained from cyanuric acid and urea mixture is 0.77 and can therefore be represented by the formula (g-C_3N_4)O.

Here are submitted the IR spectra of synthesized (from cyanuric acid and urea mixture) carbon nitride (SCN) and water-soluble carbon nitride oxide (CNO) (Fig. 4, curves *1* and *2* respectively). First of all, it is important to note, that in IR spectra of all samples distinctly there is an intensive band near 805 cm^{-1} as most

characteristic for both carbon nitride and carbon nitride oxide [26]. This band is caused by a «breathing» (bending) vibration of the triazine ring. The IR spectra also contain a range of distinct intensive absorption bands in the interval of 1200–1650 cm^{-1}, which usually are present in the IR spectra of g-C$_3$N$_4$ and (g-C$_3$N$_4$)O [26]. These bands correspond to the stretching vibrations of aromatic CN-bonds in heptazine (C$_6$N$_7$) fragments.
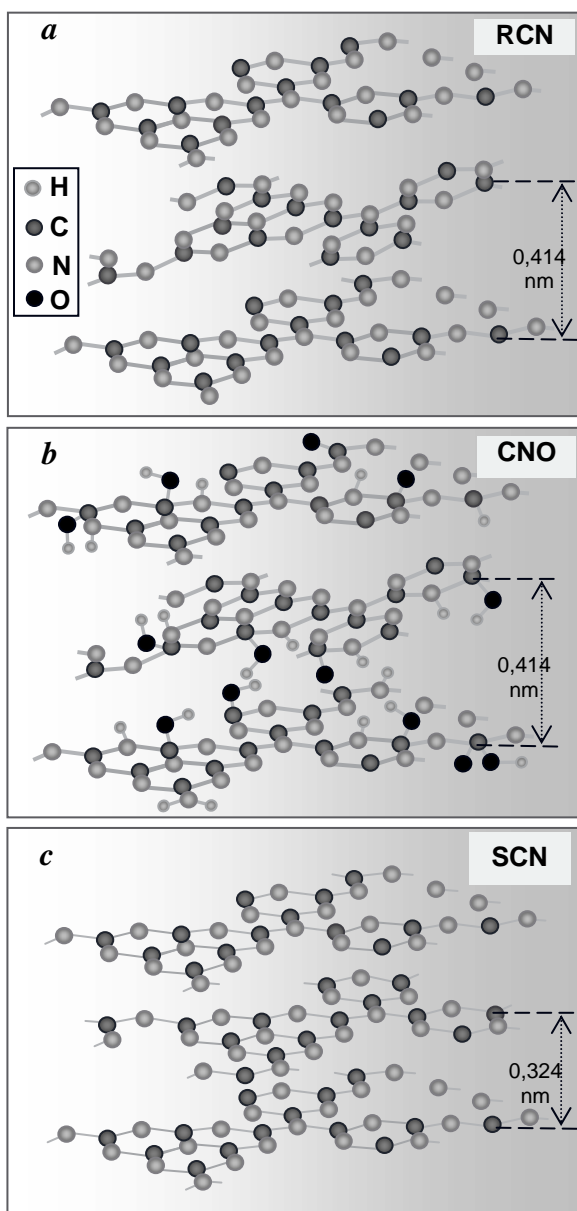
Fig. 3. Schematic atomic model of the layers and interplanar distances between adjacent layers of synthesized carbon nitride (RCN) (*a*), carbon nitride oxide (CNO) (*b*) and reduced carbon nitride (SCN) (*c*)
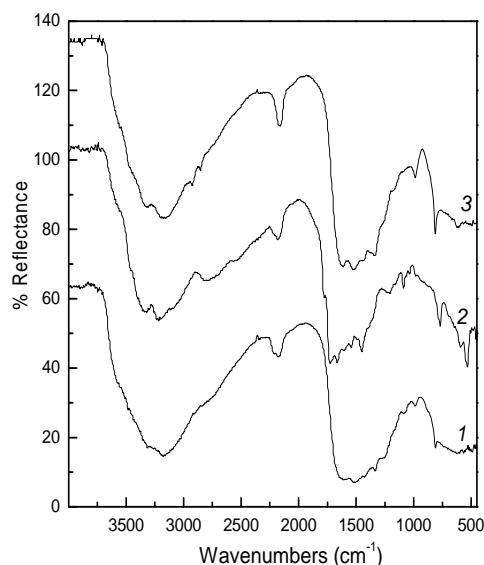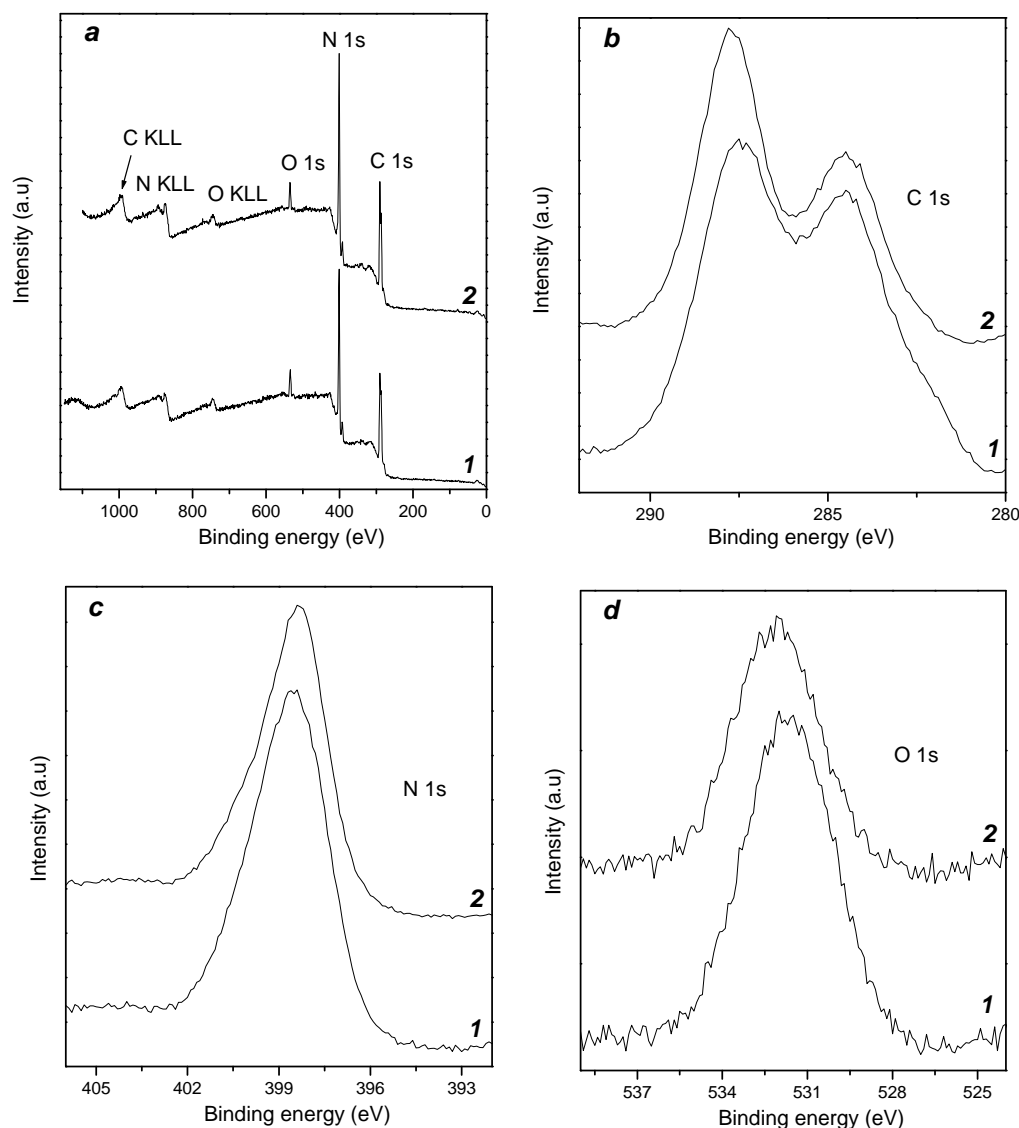
Fig. 4. IR spectra of: *1* – synthesized carbon nitride (product A), *2* – carbon nitride oxide (product B) and *3* – reduced carbon nitride (product C)

In the IR spectrum of a sample of carbon nitride oxide (product B, which contains more than 15 % oxygen) synthesized from urea-cyanuric acid (Fig. 4, curve *2*), there are absorption bands characteristic of heptazine fragments of the g-C$_3$N$_4$ structure, as well as intense bands of the –OH, >C=O and –COOH groups, which are characteristic only for both oxides of carbon nitride and graphite. (The localization of these oxygen-containing groups in the azagraphene layer is shown in Fig. 3 *b*). The peak at 1089 cm^{-1} is attributed to the stretching vibration of C-O, with together the N-H and O-H signals around 3000–3600 cm^{-1} generally related to the presence of hydroxyl groups. Most intensive signal becomes to emerge at ~ 1750 cm^{-1} for the carbon nitride oxide (product B), which suggests the formation of carbonyl (carboxyl) groups. The presence of carboxyl groups is an evidence of a stretching band at ~ 2700 cm^{-1}, characteristic for bond –O–H of carboxyl group. Note that in the IR spectrum of the synthesized carbon nitride (product A) which contains a much smaller amount of oxygen (about 5 %), the lines of oxygen-containing groups practically do not appear (Fig. 4, curve *1*).

For the first time at the reduction by hydroquinone of synthesized from urea [26] and melamine [27] carbon nitride oxide the reduced carbon nitride (or reduced multi-layer

azagraphene) was obtained [29]. Reducing of carbon nitride oxide, obtained from cyanuric acid and urea mixture, was conducted with a technique described for the reducing by hydroquinone of graphite oxide (or graphene oxide) up to graphene also. In contrast to the light-brown SCN powder (product A), reduced carbon nitride (RCN) (product C) has a dark-

brown color. According to the results of the chemical analysis, the XPS (Fig. 5) and IR (Fig. 4) spectrometry, elemental composition and chemical bonds between atoms in the heteroatomic plane of reduced carbon nitride (RCN) correspond to the bonds of synthesized carbon nitride (SCN) (Fig. 3 *a, c* respectively).

Fig. 5. XPS survey (*a*), C1*s* (*b*), N1*s* (*c*) and O1*s* (*d*) spectra of synthesized carbon nitride (product A) (curves *1*) and and reduced carbon nitride (product C) (curves *2*)

Thus, survey scan XPS spectra and C1*s*, N1*s*, O1*s* spectra of both RCN (product C) and SCN (product A) samples are substantially the same (Fig. 5). Three elements (carbon, nitrogen and oxygen) can be identified in the two samples

in the survey scan (Fig. 5 *a*). The C1*s* spectra in Figures 5 *b*, 6 *a* represent two peaks at the binding energies of ca. 284.6 and 288.0 eV, respectively. The major C1*s* peak at ~ 288 eV is identified as the tertiary carbon C-(N)$_3$ in the

g-C_3N_4 lattice. The weaker C peak at ~ 284.6 eV (which always present in the spectra of carbon nitride) is assigned to adventitious carbon species in good agreement with literature [18, 19, 31]. Asymmetry of broadened peaks C1*s* at 288–291 eV can be caused by a superposition two of peaks in this area: carbon (at ~ 288 eV) is connected with N atoms in a heptazine fragment and carbon (at ~ 290 eV) is attributed to the C bonding with O in C=O or C-O which present in O-doped carbon nitride [18, 19, 26, 33]. However, it should be noted that a presented by us earlier in [26] C1*s* peak in the X-ray photoelectron spectrum of carbon nitride oxide (CNO) containing more than 15 % oxygen is characterized by noticeable asymmetry. At the same time, in spectra of both reduced carbon nitride (product C) and synthesized carbon nitride (product A), which contain several times less oxygen (about 5 %), the asymmetry of the C1*s* peak at 288–290 eV is extremely insignificant (indicated by a circle sector in Fig. 6 *a*).

In addition, both the carbon nitride samples (products A and C) exhibit similar N1*s* profiles with core levels at around 398.5 eV which can be attributed to dicoordinated N atoms (C=N-C) in the aromatic CN heterocycles. The N1*s* region in presented by us earlier in [26] the X-ray photoelectron spectrum of carbon nitride oxide (CNO) can be fitted into three peaks, which can be ascribed to sp^2-hybridized nitrogen C=N−C (398.5 eV), sp^3-hybridized tertiary nitrogen N-$(C)_3$ (400.1 eV) and N−H groups (401.2 eV), respectively [18, 19, 31]. The deconvolution of the both N1*s* spectra of reduced carbon nitride (product C) (Fig. 6 *b*) and synthesized carbon nitride (product A) showed the presence of two main maxima. The N1*s* binding energies at about 398.5 and 399.8 eV in the high-resolution N1*s* XPS spectra of the both reduced carbon nitride (Fig. 6 *b*) and synthesized carbon nitride samples can be assigned to sp^2-hybridized nitrogen (C=N−C) and tertiary nitrogen (N-$(C)_3$) atoms, respectively (Fig. 5 *c*). O1*s* signals (Fig. 5 *d*) show a broad peak at binding energy of ca. 532 eV, which corresponds to N-C-O in O-doped carbon nitride as reported in [18, 19, 26, 33]. Interestingly, the intensity of O1*s* peak of RCN (product C) is slightly weaker than that of SCN (product A), indicating less abundant O atoms in SCN, that good agree with elemental chemical analysis results. Indeed,

according to the results of the chemical analysis, the samples SCN and RCN contain 5.7 and 4.9 % oxygen, respectively, whereas the C/N ratio in both samples is the coincide.
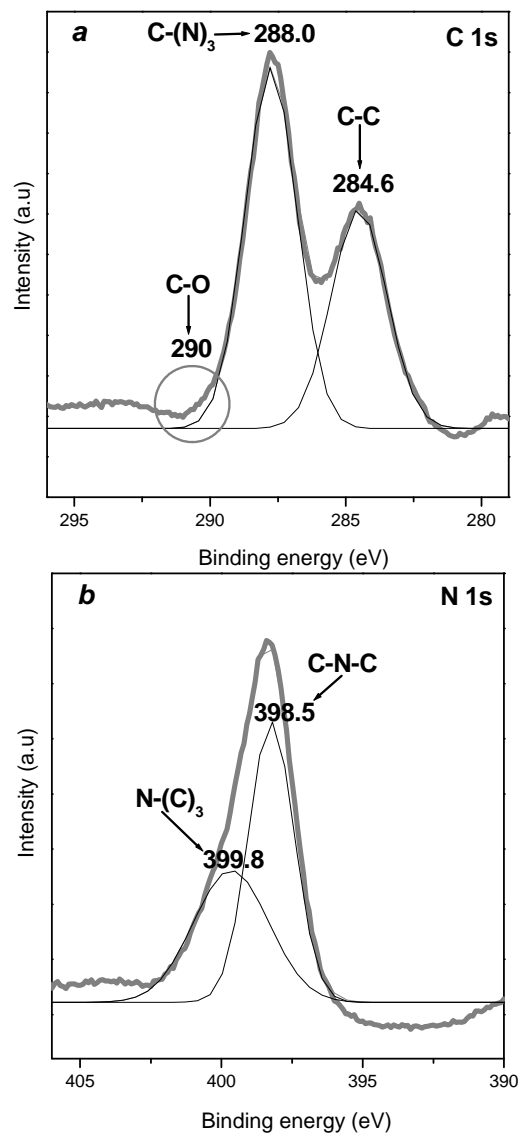
Fig. 6. High-resolution XPS spectra of C1*s* (*a*) and N1*s* (*b*) for the reduced carbon nitride (RCN) (product C)

The IR spectrum of the RCN (product C) (Fig. 4, curve *3*) corresponds almost completely to the IR spectrum of the synthesized g-C_3N_4 (product A) (Fig. 4, curve *1*), since it contains all the absorption bands in the 1200–1650 cm^{-1} region and the band near ~ 805 cm^{-1}, which are characteristic of g-C_3N_4. It is important to note that the absorption bands of oxygen-containing groups, characteristic both for (g-C_3N_4)O (product B) (Fig. 4, curve *2*) and for graphite

oxide, are practically absent in the IR spectrum of the reduced carbon nitride (product A). Therefore it is possible to consider that at the reduction of CNO (Fig. 3 *b*) reduced carbon nitride is formed (RCN) (Fig. 3 *a*) which, in particular, as for the structure of an arrangement of azagraphene layers should differ from the structure of directly synthesized carbon nitride (SCN) (Fig. 3 *c*). Really, in the XRD spectra of RCN (Fig. 1, curve *3*) practically there is only one (from three peaks characteristic for CNO) peak at $2\theta = 21.49\,°$, which in a XRD spectrum of $(g\text{-}C_3N_4)O$ (Fig. 1, curve *2*) corresponds to the increased interplanar distance. At the same time, the peak at $2\theta = 27.49\,°$ ($d = 0.324$ nm) describing the distance between the heptazine layers of synthesized carbon nitride (SCN) (Fig. 1, curve *1*) in a XRD pattern of reduced carbon nitride RCN is very weak. In the XRD of RCN sample (Fig. 1, curve *3*) also there is no peak at $2\theta = 10.76\,°$, which is characteristic for CNO (Fig. 1, curve *2*), but there is a peak at $2\theta = 12.40\,°$, describing in-planar repeating unit with a period of 0.714 nm in $g\text{-}C_3N_4$ (Fig. 1, curve *1*). Hence, in RCN the in-planar distance (describing a distance between fragments (C_6N_7)) corresponds to $g\text{-}C_3N_4$, but the interplanar distance is characteristic for $(g\text{-}C_3N_4)O$. According to XRD results, reduced carbon nitride (RCN) probably consists of poorly connected heteroatomic azagraphene layers, because it has a significantly larger (on 0.09 nm) interplanar distance between the adjacent nitrogen-carbon layers than that between the layers of synthesized carbon nitride (SCN).

And finally, we would like to mention that the since the first study, culminating in the successful use of $g\text{-}C_3N_4$ in the photocatalytic production of H_2 from H_2O in 2009 [6], there has been an exponential growth in scientific research on materials based on $g\text{-}C_3N_4$. Currently, the research aimed at developing photocatalysts based on nanostructured and doped $g\text{-}C_3N_4$ occupies flagship positions in order to meet the global demand for renewable energy sources (hydrogen production by photocatalytic H_2O splitting) and to solve the problem of environmental pollution (photocatalytic conversion of carbon dioxide CO_2 into energy carriers) [2–5, 7–9].

CONCLUSIONS

Graphite-like carbon nitride (and its nanostructured and doped derivatives) is one of the most promising photocatalysts. The oxygen-doped carbon nitride ($O\text{-}g\text{-}C_3N_4$) and carbon nitride oxide ($(g\text{-}C_3N_4)O$) was simultaneously synthesized by the gas phase method under special reaction conditions of pyrolysis of cyanuric acid and urea mixture. Reduced carbon nitride (with poorly connected heteroatomic azagraphene layers), in which as against synthesized carbon nitride the interplanar distance between the adjacent nitrogen-carbon layers is increased on 0.09 nm, was obtained due to reduction by hydroquinone of the water-soluble carbon nitride oxide, obtained from cyanuric acid-urea mixture.

Синтез багатошарового азаграфена та оксиду нітриду вуглецю

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Графітоподібний нітрид вуглецю (що характеризується як нетоксичний і хімічно високостійкий матеріал) і його наноструктуровані і доповані, зокрема, киснем, похідні, привертають особливу увагу в якості найбільш перспективних матеріалів зеленої енергетики як фотокаталізатори для виробництва водню з поновлюваних, природних джерел (вода, парниковий газ) і відновлення навколишнього середовища шляхом деградації токсичних органічних забруднювачів. Актуальним завданням для розширення сфери застосування g-C₃N₄ є покращення і оптимізація його каталітичних, електронних і оптичних властивостей, як за допомогою збільшення площі поверхні, так і за рахунок збільшення числа активних центрів

нітридвуглецевої площини внаслідок допування графітоподібного нітриду вуглецю. Використання суміші двох різних прекурсорів забезпечує створення гетеропереходів і, як наслідок, покращання фотокаталітичних характеристик g-C₃N₄. Допований киснем нітрид вуглецю (O-g-C₃N₄) і водорозчинний оксид нітриду вуглецю (g-C₃N₄)O одночасно синтезували газофазним методом в особливих реакційних умовах піролізу суміші ціанурової кислоти і сечовини. Наноструктурований відновлений нітрид вуглецю (або відновлений багатошаровий азаграфен) отримували за допомогою відновлення гидрохиноном оксиду нітриду вуглецю (g-C₃N₄)O. Отримані продукти були досліджені методами інфрачервоної (ІЧ) і рентгенівської фотоелектронної (РФЕ) спектроскопії, хімічного і рентгенофазового (РФА) аналізу, скануючої електронної мікроскопії (СЕМ). Відповідно до результатів РФЕ і ІЧ спектрометрії, хімічні зв'язки між атомами в гетероатомній площині відновленого нітриду вуглецю (ВНУ) відповідають зв'язкам в синтезованому нітриді вуглецю (СНУ). Однак, згідно з результатами РФА, вважаємо, що відновлений нітрид вуглецю (ВНВ) складається з слабкоп'язаних гетероатомних шарів азаграфену, оскільки він має значно більшу (на 0.09 нм) міжплощинну відстань між сусідніми азот-вуглецевими шарами, ніж така між шарами синтезованого нітриду вуглецю (СНВ). Методом СЕМ встановлено, що піроліз суміші різних прекурсорів (цианурової кислоти і сечовини) дає продукт з меншими кристалічними доменами (що може поліпшити фотокаталітичні характеристики), ніж піроліз одного прекурсора (сечовини).

Ключові слова: *азаграфен, оксид нітриду вуглецю, цианурова кислота, сечовина, піроліз, фотокаталізатор*

Синтез многослойного азаграфена и оксида нитрида углерода

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Графитоподобный нитрид углерода (характеризующийся как нетоксичный и химически высокостойкий материал) и его наноструктурированные и допированные, в частности, кислородом, производные, привлекают особое внимание в качестве наиболее перспективных материалов зеленой энергетики как фотокатализаторы для производства водорода из возобновляемых, природных источников (вода, парниковый газ) и восстановления окружающей среды путем деградации токсичных органических соединений. Актуальной задачей для расширения сферы применения g-C₃N₄ является улучшение и оптимизация его каталитических, электронных и оптических свойств, как посредством увеличения площади поверхности, так и за счет увеличения числа активных центров нитридуглеродной плоскости вследствие допирования графитоподобного нитрида углерода. Использование смеси двух разных прекурсоров обеспечивает создание гетеропереходов и, как следствие, улучшение фотокаталитических характеристик g-C₃N₄. Допированный кислородом нитрид углерода (O-g-C₃N₄) и водорастворимый оксид нитрида углерода (g-C₃N₄)O одновременно синтезировали газофазным методом в особых реакционных условиях пиролиза смеси цианурной кислоты и мочевины. Наноструктурированный восстановленный нитрид углерода (или восстановленный многослойный азаграфен) получали посредством восстановления гидрохиноном оксида нитрида углерода (g-C₃N₄)O. Полученные продукты были исследованы методами (ИК) и рентгеновской фотоэлектронной (РФЭ) спектроскопии, химического и рентгенофазового (РФА) анализов, сканирующей электронной микроскопии (СЭМ). В соответствии с результатами РФЭ и ИК спектрометрии химические связи между атомами в гетероатомной плоскости восстановленного нитрида углерода (ВНУ) соответствуют связям в синтезированном нитриде углерода (СНУ). Однако, согласно результатам РФА, полагаем, что восстановленный нитрид углерода (ВНУ) состоит из слабосвязанных гетероатомных слоев азаграфена, поскольку он имеет значительно большее (на 0.09 нм) межплоскостное расстояние между соседними азот-углеродными слоями, чем между слоями синтезированного нитрида углерода (СНУ). Методом СЭМ установлено, что пиролиз смеси различных прекурсоров (цианурной кислоты и мочевины) дает продукт с меньшими кристаллическими доменами (что может улучшить фотокаталитические характеристики), чем пиролиз одного прекурсора (мочевины).

Ключевые слова: *азаграфен, оксид нитрида углерода, цианурная кислота, мочевина, пиролиз, фотокатализатор*

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