

## Direct synthesis of O-doped Carbon Nitride and Oxide of Graphite-like Carbon Nitride from Melamine

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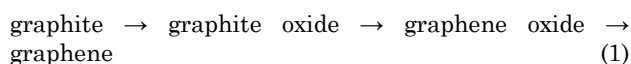
It was first performed a special method of pyrolysis of melamine in order to study the possibility of co-production of carbon nitride and its oxidized derivatives. New compound as a graphite-like carbon nitride oxide (g-C<sub>3</sub>N<sub>4</sub>)O, which is isostructural analogue of graphite oxide, and doped with oxygen (~8.1%), carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) were obtained. In contrast to known methods for the preparation of samples doped with oxygen carbon nitride a new route does not provide a preliminary synthesis of g-C<sub>3</sub>N<sub>4</sub>. The synthesized carbon nitride oxide is easily stratified and dissolved in water to form a flocculent solution which may contain not only ultra-thin nanosheets from several heptazine oxidized layers, but also the individual two-dimensional monolayers. These monolayers can be a precursor for making reduced heptazine monolayer (or azagraphene). The synthesized substances were investigated by methods chemical and X-ray analyses, IR spectroscopy, temperature-programmed desorption mass spectrometry (TPDMS) obtained products.

**Keywords:** O-doped carbon nitride, Oxide of graphite-like carbon nitride, Pyrolysis, Synthesis, Melamine.

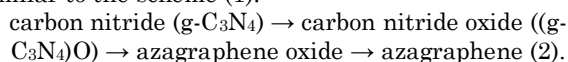
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### 1. INTRODUCTION

Graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) as one of the most promising materials in green energy has been used successfully as an efficient photocatalyst. However photoactivity doped by oxygen the carbon nitride is 7 times higher than the undoped g-C<sub>3</sub>N<sub>4</sub>, and the boundary photoactivity O-C<sub>3</sub>N<sub>4</sub> in the visible spectrum extends from 460 to 498 nm [1]. Therefore, the increased interest in modifying carbon nitride with oxygen is well founded. Therefore, we can assume that the existing route of the preparation of graphene from graphite



would also most suitable for the synthesis from carbon nitride of its dimensional monolayers consisting of tri-s-triazine (heptazine C<sub>6</sub>N<sub>7</sub>) fragments linked nitrogen bridges. By analogy with azafullerene (C<sub>59</sub>N), wherein in a fullerene structure only one carbon atom replaced by a nitrogen atom, a hypothetical heteroatomic (C<sub>6</sub>N<sub>8</sub>)<sub>n</sub> monolayer from the structure of carbon nitride can be called azagraphene (or heptazinic graphene). Hence, synthesis of the hypothetical azagraphene from graphitic carbon nitride can be represented a scheme (2) similar to the scheme (1):



It is known [1] that carbon nitride unlike graphite is partially oxidized in the aqueous solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Therefore currently doped oxygen carbon nitride prepared by only two stage method at an oxidation by H<sub>2</sub>O<sub>2</sub> previously synthesized g-C<sub>3</sub>N<sub>4</sub>.

Noticeable dissolution and stratification of g-C<sub>3</sub>N<sub>4</sub> nanosized particles (to form ultrathin nanosheets) have been performed only in concentrated alkaline solutions

at 50-90°C and in the absence of reducing agents by "green" peeling liquid [2]. (Note that this method is used to obtain stable suspensions of graphene from exfoliated graphite oxide.) Compared with the insoluble carbon nitride its nanosheets have increased photoabsorption and photoresponse, are used as non-metal biosensor. The information on obtaining carbon nitride oxide to date in the literature is absent.

We believe that the carbon nitride oxide may be formed in parallel with the synthesis of carbon nitride by thermal transformation of melamine (cyanamide or dicyandiamide) molecules (or fragments of their degradation) into heptazine layers. In this work it was first investigated particular melamine pyrolysis method to obtain carbon nitride along with its oxidized derivatives.

### 2. EXPERIMENTAL

Earlier we through the author method [3-5] of pyridine pyrolysis [6] has been prepared a doped with oxygen (11.1 mass% O) low nitrogen content carbon nitride (O-C<sub>3</sub>N). Onion nanostructures of turbostratic carbon nitride formed in the reactionary vapour-gas stream easily oxidized in air to O-C<sub>3</sub>N. In this study, a similar approach is used for obtaining of carbon nitride and its oxidized derivatives during the thermal transformation of melamine molecules. The studies were performed by varying the amount of melamine, the temperature and the duration of its heat treatment. Comparing products obtained under fixed reactionary conditions of pyrolysis evaluated for their quantity, chemical (carbon, nitrogen, oxygen, and hydrogen) and X-ray analysis. This paper presents the results of a study of the pyrolysis products of melamine, which, according to X-ray analysis contain carbon nitride, but do not contain the original melamine. Synthesized substances have been investigated by methods chemical and X-ray analyses, IR

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spectroscopy, temperature-programmed desorption mass spectrometry (TPDMS) formed products.

### 3. RESULTS AND DISCUSSION

In particular amount of melamine by varying of the temperature and duration of pyrolysis was defined temperature range in which the resultant reaction product is substantially (according to X-ray diffraction) contained no phase precursor. In our experimental conditions the conversion of melamine in the carbon nitride is begun at 520°C: in the X-ray spectrum (Fig. 1, curve 4) of a resultant product A0 of pyrolysis on a background of intense lines belonging melamine are presented noticeable enough reflexes at  $2\theta = 12.40$  and  $27.49$ , those are characteristic for graphitic carbon nitride. At temperatures above 550°C phase of melamine into pyrolysis products A1 (Fig. 1, curve 3) and B1 is not detected at all. However, from the X-ray diffraction patterns may see that the phase composition of obtained at different temperatures resultant products are markedly different and, hence, the route of melamine conversion depends on its pyrolysis the temperature.

A brown powdery product A1 (Fig. 1, curve 3) is formed at melamine pyrolysis at 550°C, in which X-ray spectrum clearly are detected four reflex, two of which ( $2\theta = 12.40^\circ$  and  $2\theta = 27.49^\circ$ ) completely are characteristic for g-C<sub>3</sub>N<sub>4</sub>, respectively for the planes 100 ( $d = 0.714$  nm) and 002 ( $d = 0.324$  nm). The presence in the X-ray spectrum of the sample A1 of additional low-intensity peaks at  $2\theta = 21.45^\circ$  and  $10.79^\circ$  may indicate the presence in the product of the pyrolysis of other O, C, N-containing phases. Indeed, the sample A1, unlike carbon nitride of formula composition partially dissolved in hot water to form an intensely colored yellow solution B2. Diffractogram of insoluble brown powder A2 (Fig. 1, curve 2), on which there are two characteristic for carbon nitride reflex, fully consistent with both the calculated and experimental [7] X-ray spectra of the g-C<sub>3</sub>N<sub>4</sub>. Indeed, the sample A2 by elemental chemical analysis contains 35.9 mass% carbon, 54.7 mass% nitrogen, 1.3 mass% hydrogen and 8.1 mass% oxygen, which may correspond to carbon nitride (C<sub>3</sub>N<sub>3.92</sub>H<sub>1.30</sub>O<sub>0.51</sub>) with a ratio C/N (0.765) close formula (0.75). Consequently, during the pyrolysis of melamine doped by oxygen carbon nitride is formed.

Sample B2, which is formed after evaporation of water, has a yellow color. Its diffraction pattern (Fig. 1, curve 1) there are three reflex at  $2\theta = 10.79$ ,  $21.45$  and  $27.49^\circ$ , which are probably inherited from the original sample A1. We can assume that in this sample is realized unidirectional shift both interplanar spacings in the direction of their increase in comparison with the carbon nitride sample A2. Consequently, during the pyrolysis of melamine, together with oxygen-doped carbon nitride is formed a water-soluble substance B2, which may correspond to carbon nitride oxide, the X-ray spectrum (Fig. 1, curve 1) which is presented here for the first time.

At higher temperatures (particularly at 580°C) pyrolysis of melamine is formed yellow product B1, which has XRD patterns identical to the diffraction pattern of the sample B2: three reflexes at  $2\theta = 10.79$ ,  $21.45$  and  $27.49^\circ$  are characteristic for sample B2. In accordance

with the chemical composition (49.6% nitrogen, 1.5% hydrogen, 16.1% oxygen and 32.8% carbon) sample B1 can be represented as formula C<sub>3</sub>N<sub>3.89</sub>H<sub>1.65</sub>O<sub>1.09</sub>. It can be seen that the product B1 compared to sample A2 contains twice more oxygen, while the ratio C/N in which approximately comparable, 0.771 and 0.765 respectively. Sample B1 unlike A1 completely dissolves in hot water to form a flocculent yellow solution from which after an evaporation of water yellow powder B3 is precipitated. (The flocculent solution containing nanosheets (2-4 nm thick) of carbon nitride is formed by ultrasonic peeling in the acid powdery g-C<sub>3</sub>N<sub>4</sub> [2]). Thus, three reflex at  $2\theta = 10.79$ ,  $21.45$  and  $27.49^\circ$  in the diffraction patterns of recrystallized yellow powder B3 coincide with the reflections in the diffraction patterns of samples B1 and B2.

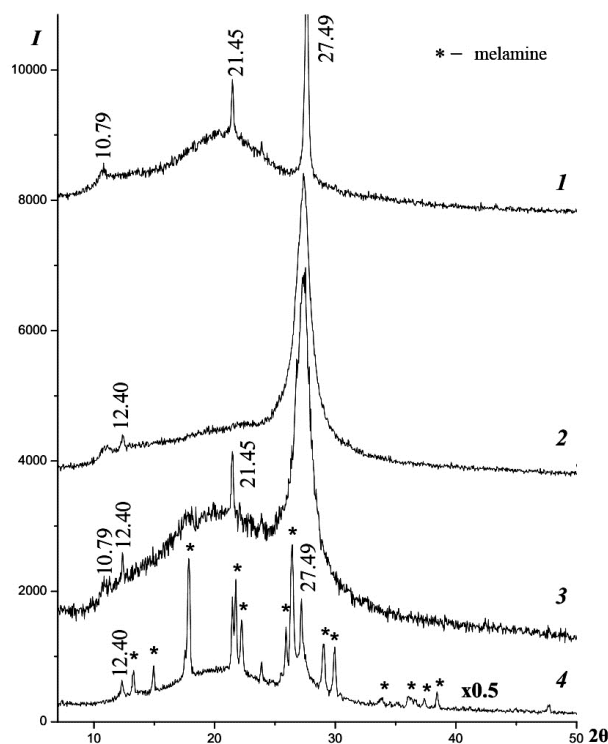


Fig. 1 – XRD patterns of samples B2 (1), A2 (2), A1 (3), A0 (4)

When comparing the diffraction patterns of water-insoluble oxygen-doped carbon nitride C<sub>3</sub>N<sub>3.92</sub>H<sub>1.30</sub>O<sub>0.51</sub> (sample A2, 8.1mass% O) and water-soluble substantially more oxidized carbon nitride (sample B1 (16.1 mass% O) as well as B2) clearly may see that the structure of their X-ray spectra differ markedly. The spectrum of sample B1 there is a significant shift of the signal corresponding to the interaction between heptazine fragments in a monolayer, with  $12.40^\circ$  to  $10.79^\circ$ . Thus, the most intense signal at  $2\theta = 27.49^\circ$ , characterizing interlayer interaction g-C<sub>3</sub>N<sub>4</sub>, is maintained. Furthermore, there is a new reflex at  $2\theta = 21.45^\circ$  in XRD patterns B1, not present in the spectrum of the sample A2 (and g-C<sub>3</sub>N<sub>4</sub>). It can be assumed that the obtained water-soluble product B1, containing 16.1% oxygen and having an X-ray spectrum differs from the spectrum of g-C<sub>3</sub>N<sub>4</sub>, corresponds to a new compound, carbon nitride oxide (g-C<sub>3</sub>N<sub>4</sub>O). We believe that the observed changes (compared to carbon nitride) in structure of carbon nitride oxide associated with features (compared to the

structure of graphite oxide) of location of heteroatoms (N and O) in the plane heptazine layer.

Each plane of graphite oxide is a continuous graphene network and any oxygen-containing groups (hydroxyl or epoxy) can only be located between the graphene layers, which leads to such a large increase in the interlayer spacing from 0.34 nm in the graphite to about 0.7 nm in the graphite oxide. Therefore in the X-ray spectrum of graphite oxide signal at  $2\theta = 26^\circ$  characteristic for graphite virtually disappears, and the halo appears at the  $2\theta = 10-15^\circ$ . However heteroatomic (nitrogen-carbon) plane of *g*- $C_3N_4$  has not continuous but "openwork network" because it consists of heptazine  $C_6N_7$  fragments connected nitrogen bridges. Thus, in a plane between adjacent heptazine fragments exist the voids with diameter 0.717 nm (Fig. 2a). In the space of this void can be freely placed two oxygen-containing groups, in which the bond lengths are  $\sim 0.143$  nm (C–O) and  $\sim 0.091$  nm (O–H). (Note that in the carbon nitride oxide ( $C_3N_4$ )O to six carbon atoms heptazine fragments have two oxygen atoms). Moreover, the oxidation of carbon nitride may also accompanied by some gap between heptazine bonds and nitrogen-bridged fragments (Fig. 2b), which leads to an increase in the distance between the heptazine blocks with 0.717 ( $2\theta = 12.40^\circ$ ) to 0.818 ( $2\theta = 10.79^\circ$ ) nm.

However, in the carbon nitride oxide interlayer spacing close to the characteristic (0.324 nm ( $2\theta = 27.49^\circ$ )) for carbon nitride can be partially preserved in some parts of heptazine planes due to the distortion of the planarity in the opening of the double bonds ( $-C=N- \rightarrow -C(OH)-NH-$ ) in heterocycles. This "fluting" heptazine cell in carbon nitride oxide may be the cause of additional peak at  $2\theta = 21.45^\circ$ , corresponding substantially greater (compared with carbon nitride) interplanar spacing, 0.414 nm.

Thus, carbon nitride oxide (*g*- $C_3N_4$ O) although it is a structural analog of graphite oxide, however, due to voids in heptazine planes and localization features therein oxygen (or OH groups) interplanar distance in (*g*- $C_3N_4$ )O slightly (by 0.09 nm) increases only in certain areas of these planes. We believe that the infrared spectrum of carbon nitride oxide must necessarily contain both bands characteristic for vibrations of a heptazine layer of carbon nitride and the oxygen-containing functional groups of bands that present in the IR spectrum of graphite oxide, but absent in the IR spectrum of *g*- $C_3N_4$ .

IR spectra of the samples A2, B1 and B3 (Fig. 3, curves 3, 2 and 1, respectively) contain a number of distinct intense absorption bands in the region 1200–1650  $cm^{-1}$ , which correspond to characteristic for *g*- $C_3N_4$  stretching vibrations of aromatic CN- bonds in the heptazine ( $C_6N_7$ ) fragments of carbon nitride [7]. The spectra of all three samples contain the characteristic peak at 810  $cm^{-1}$ , corresponding to the "breathing" vibration of triazine ring ( $C_3N_3$ ). In contrast the IR spectra of samples *g*- $C_3N_4$ , obtained by known methods, in the IR spectra of A2, B1 and B3 is present the absorption bands of hydroxyl group. The absorption band at 1185  $cm^{-1}$  corresponds to C–O bond of hydroxyl group, but broad strong absorption bands at about 3200 and 3300  $cm^{-1}$  correspond to the stretching vibrations of –OH and –NH groups respectively.

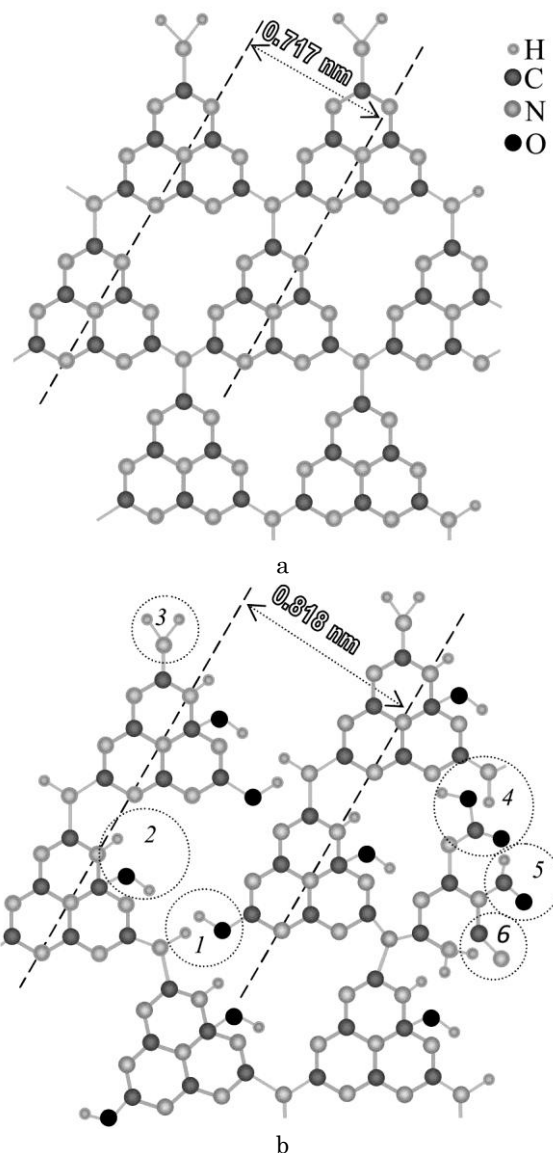


Fig. 2 – Schematic atomic model of *g*- $C_3N_4$  (a), (*g*- $C_3N_4$ )O (b)

It is important to note that in almost identical IR spectra of water-soluble samples (B1 and B3) of carbon nitride oxide presents at 1728  $cm^{-1}$  intense absorption band carbonyl (carboxyl) terminal groups, whereas in the IR spectrum of O-*g*- $C_3N_4$  (A2), which comprises in 2 times (8.1 %) less amount of oxygen, this absorption band completely absent. In the presence of carboxyl groups in IR spectra of samples B1, B3 indicates also broadened band at  $\sim 2700$   $cm^{-1}$ , characteristic for –O–H bonds of the carboxyl group. Furthermore, in the IR spectra of samples B1, B3 weaker signals are present at  $\sim 1270$ , 970 and 780  $cm^{-1}$ , which may reflect the characteristic stretching vibrations of the epoxy group. It is noteworthy that the absorption bands characteristic for given oxygen-containing groups (hydroxyl, epoxy, carbonyl and carboxyl) are always present in the IR spectra of graphite oxide. Consequently, the IR spectrum of the sample synthesized carbon nitride oxide is original since it contains additional bands which are absent both in the known samples of *g*- $C_3N_4$  and oxygen doped carbon nitride.

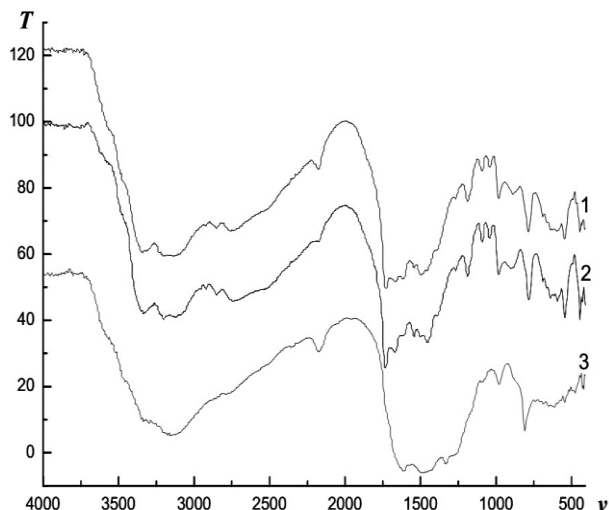


Fig. 3 – FTIR spectra of samples B3 (1), B1 (2) and A2 (3)

The synthesized sample of the water-soluble carbon nitride oxide compared to carbon nitride of formula composition naturally is less thermally stable. The main feature of the thermal decomposition of carbon nitride oxide (Fig. 4), as well as carbon nitride doped with oxygen is the presence in the composition of the gaseous products of their thermolysis both nitrogen-carbon ( $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{C}_2\text{N}_2$ ), and oxygen containing ( $\text{NCO}$ ,  $\text{NCOH}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ) fragments. The data fragments that are detected at a temperature of thermolysis  $\sim 300^\circ\text{C}$  are formed, probably, due to the destruction of functional groups arranged in layers defects. Evacuation of cyanogen at thermolysis of  $(g\text{-C}_3\text{N}_4)\text{O}$  and  $\text{O-g-C}_3\text{N}_4$  indicates on complete destruction of heptazine nitride-carbon layer, which is begun (according to mass spectrometric data) for both samples at  $\sim 600^\circ\text{C}$ . It should to note that known examples of carbon nitride (obtained from precursors such as dicyandiamide or melamine [8]) is completely decom-

posed in a nitrogen atmosphere in the temperature range  $600\text{-}800^\circ\text{C}$  with evacuation of  $\text{C}_2\text{N}_2$ ,  $\text{CNH}_2$  and  $\text{NH}_3$ . However ions of  $\text{CNH}_2^+$  and  $\text{NH}_3^+$  are detected in the products of thermolysis undoped carbon nitride already at about  $450^\circ\text{C}$ .

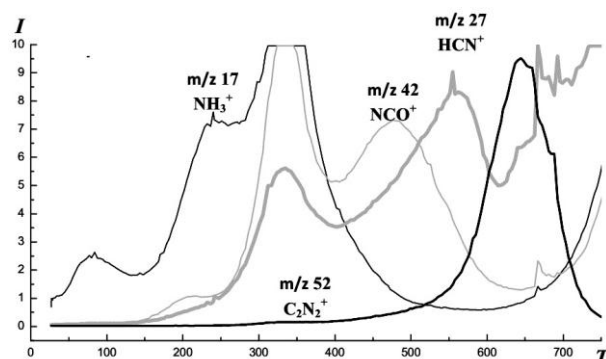


Fig. 4 – Selected thermodesorption curves of sample B1

#### 4. CONCLUSIONS

A special method of pyrolysis of melamine for obtaining of predominantly oxidized derivatives of carbon nitride is developed. This method in contrast to the known methods does not provide a preliminary synthesis of  $g\text{-C}_3\text{N}_4$ . First along with oxygen-doped ( $\sim 8.1\%$ ) carbon nitride ( $\text{O-g-C}_3\text{N}_4$ ) was obtained a new compound in the form of graphitic carbon nitride oxide ( $(g\text{-C}_3\text{N}_4)\text{O}$ ). Nano-dimensional particles of  $(g\text{-C}_3\text{N}_4)\text{O}$  is stratified and dissolved readily in water to form a flocculent solution, which, probably, may contain ultrathin nanosheets from oxidized heptazine based monolayers. We believe that the oxidized heptazine two-dimensional monolayers can be a precursor for heptazine monolayer (or azagraphene).

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