

Structural and Photoluminescence Properties of Graphite-Like Carbon Nitride

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Abstract—Interrelationship between the structure and optical properties of graphite-like semiconductor carbon nitride produced by the heat treatment of thiocarbamide in an oxygen-containing medium at temperatures in the range from 400°C to 625°C is established. It is found that the maximum of the photoluminescence band shifts from 417 to 494 nm and simultaneously broadens, as the temperature of synthesis is elevated to 625°C. This effect is attributed to doping with oxygen and to the formation of defects as a consequence of decomposition of the already synthesized material with increasing temperature.

Keywords: graphite-like carbon nitride, g -C₃N₄, structure, photoluminescence

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1. INTRODUCTION

Graphite-like carbon nitride (g -C₃N₄), which possesses semiconductor properties (band gap of $E_g \approx 2.7$ eV) [1], attracts attention due to its well-pronounced photocatalytic and luminescence properties which offer promise for practical applications [2]. As graphite, bulk g -C₃N₄ is layered in structure. Each layer consists of planar tri- s -triazine cells. The layers are bound to each other by weak van der Waals forces, which makes it possible to split the layers by many methods (thermal, ultrasonic, chemical treatments) and to obtain two-dimensional graphene-like sheets. Particular interest in the material is conditioned by the simplicity of its synthesis by the heat treatment of organic compounds with a large content of nitrogen, e.g., melamine [3, 4], cyanamide [6], dicyandiamide [6], carbamide, and thiocarbamide [7].

Previously it was shown that graphite-like carbon nitride luminesced at room temperature, which is promising for light-emitting structures [8]. It was found that the position of the photoluminescence maximum depended on the temperature of synthesis of the material [9]. The studies carried out by us [10] show that, in principle, it is possible to form graphite-like carbon nitride in porous glassy matrices, which is important for practical use of the material as a photocatalyst. It is also established that graphite-like carbon nitride is doped with oxygen [11] during synthesis in the temperature range 450–550°C. However, from the

set of currently available experimental data, it is impossible to unambiguously understand how the physical and chemical properties of the material depend on the conditions of synthesis. Thus, the purpose of these studies is to judge the influence of the temperature of synthesis of g -C₃N₄ from thiocarbamide in the range 400–625°C on the structural and luminescence properties of the material.

2. EXPERIMENTAL

Thiocarbamide (CS(NH₂)₂ (brand “pure for analysis” (PFA)) in the amount of 2 g was put into a purified ceramic crucible with a volume of 20 mL, with subsequent hermetic sealing in order to reduce the outflow of gases from the crucible during decomposition of the precursor and to restrict the access for air to the material synthesized. Heat treatment was conducted in a muffle furnace at a specified temperature in the range 400–625°C for 30 min. The average rate of heating of the furnace from room temperature to the temperature of synthesis was 12°C min⁻¹. After the completion of synthesis, the furnace naturally cooled to a temperature close to room temperature.

The morphological properties of the material were studied by scanning electron microscopy (SEM) using a Hitachi S-4200 microscope. To determine the crystal structure and phase composition, we used X-ray diffraction (XRD) analysis; the XRD measurements were conducted with a DRON-4 diffractometer (the

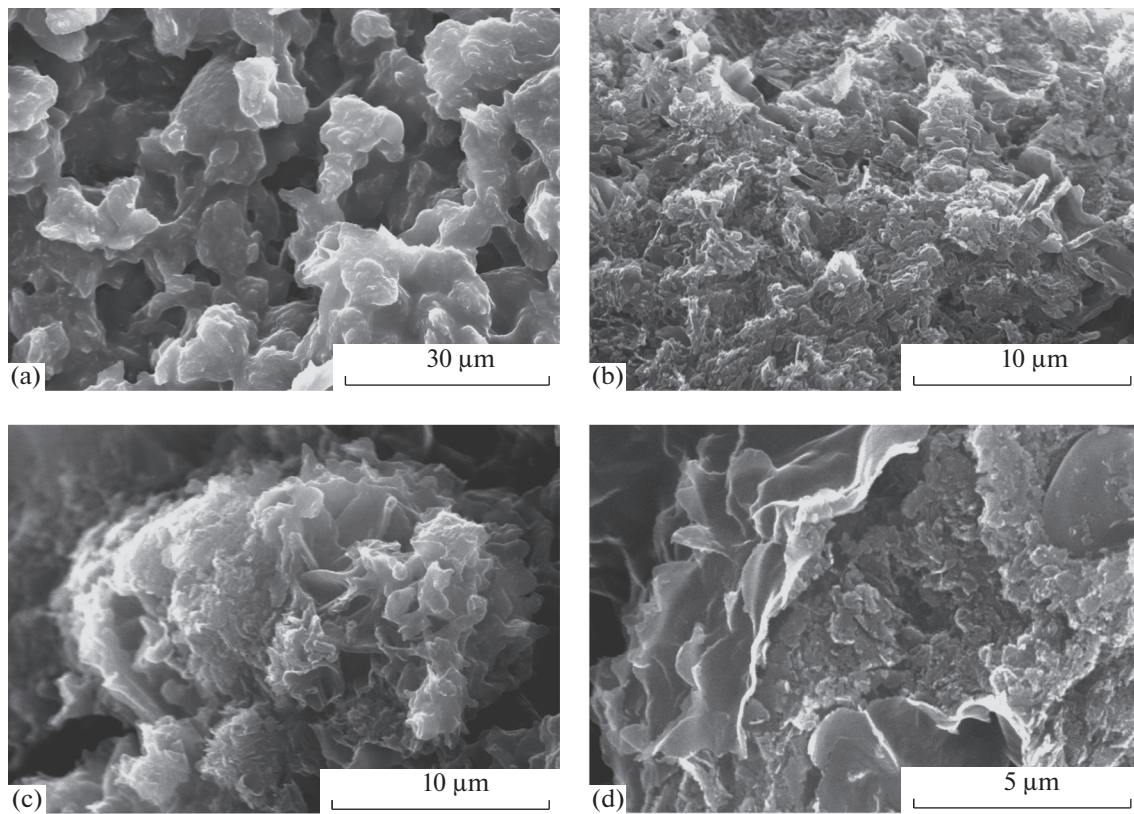


Fig. 1. Surface of the material synthesized by the heat treatment of thiocarbamide for 30 min at (a) 450°C, (b) 500°C, (c) 550°C, and (d) 600°C.

radiation wavelength $\lambda = 0.154184$ nm). Chemical bonding in the material was studied by Fourier transform infrared (FTIR) spectroscopy, using a Bruker Vertex 70 FTIR spectrometer. The photoluminescence (PL) of the material was studied upon excitation with monochromatic radiation at the wavelength 345 nm at room temperature; the 345-nm line was separated out from the emission of a xenon lamp with the power 1 kW, using a Solar TII DM 160 monochromator. The PL spectrum was recorded with a Solar TII MS 7504i monochromator spectrograph equipped with a silicon CCD matrix.

3. RESULTS

The surface structure of the material synthesized in the study is shown in Fig. 1. The heat treatment of thiocarbamide at 400°C and 450°C brings about the formation of a finely dispersed material that consists of coarse particles with a molten surface. The dimension of the particles is ~ 20 μm , and the spacing between them is ~ 15 μm (Fig. 1a). In turn, these particles are formed from particles 3–5 μm in dimensions. An increase in the treatment temperature results in compaction of the structure and in the transition from a coarse-grained structure to a mixed structure

composed of 500- to 700-nm-thick wafers built into submicron grains (Figs. 1a–1d).

The XRD analysis performed in the study shows that the synthesized material is $g\text{-C}_3\text{N}_4$; the typical XRD spectrum is shown in Fig. 2. Characteristic peaks are observed at the angles 13.2°, 27.7°, 44.2°, and 56.2°.

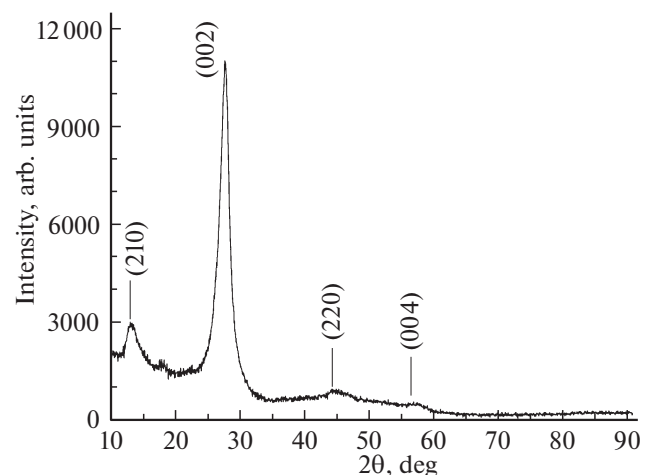


Fig. 2. XRD pattern of $g\text{-C}_2\text{N}_4$ synthesized at 500°C for 30 min.

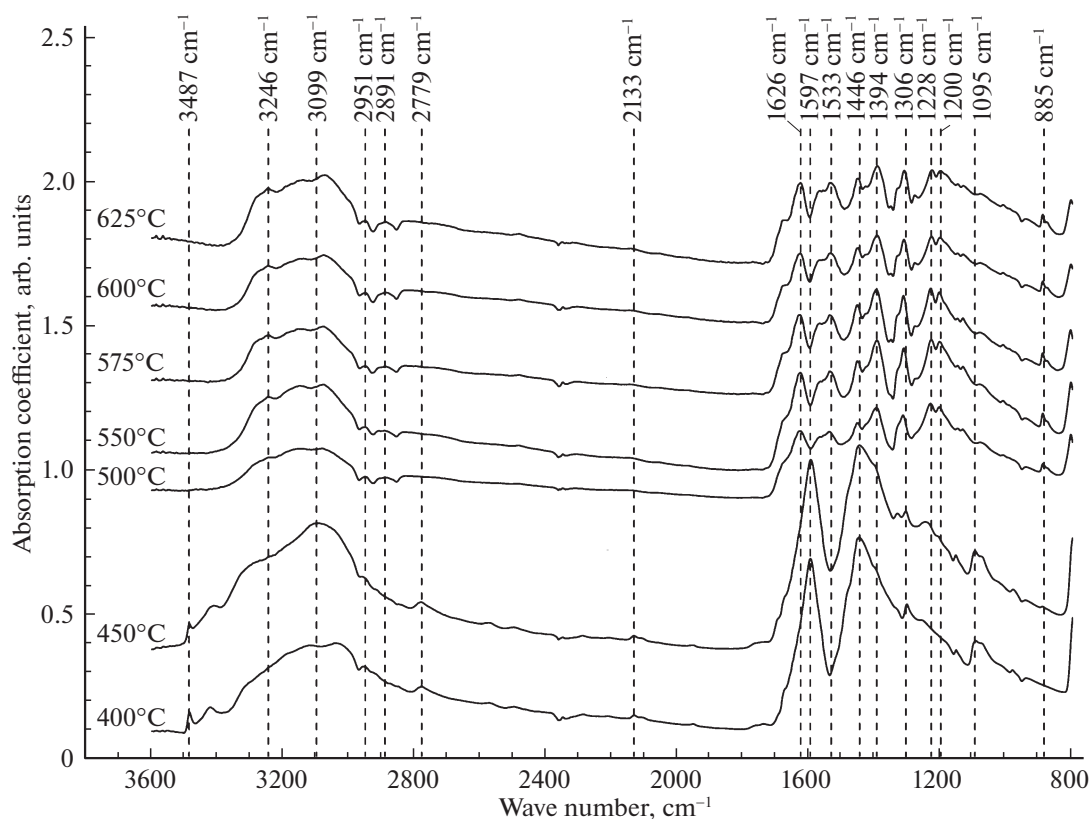


Fig. 3. FTIR spectra of materials synthesized from thiocarbamide at different temperatures for 30 min.

and 57.1° corresponding to the (210), (002), (220), and (004) crystallographic planes of $g\text{-C}_3\text{N}_4$, respectively [12]. The crystallite size estimated from the (210) and (002) reflection widths is ~ 5 nm.

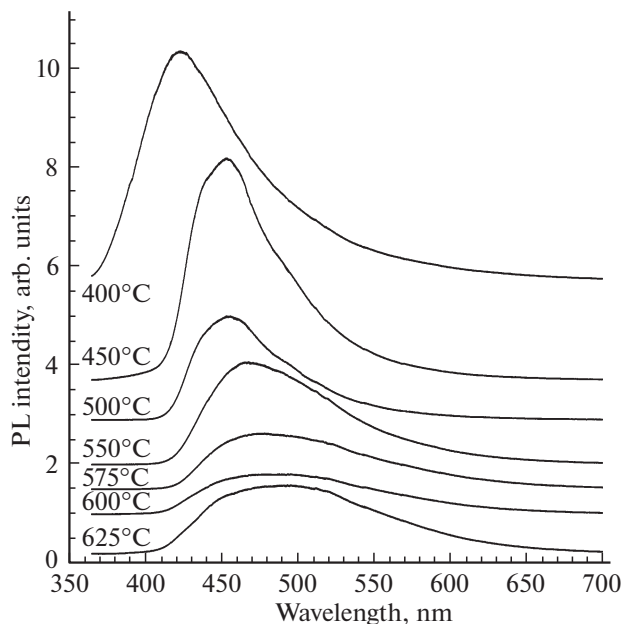


Fig. 4. PL spectra of materials synthesized from thiocarbamide at different temperatures for 30 min.

The results of FTIR studies of the material synthesized at different temperatures (Fig. 3) confirm the inference about the formation of $g\text{-C}_3\text{N}_4$. Specifically, absorption in the range $2700\text{--}3500\text{ cm}^{-1}$ is commonly attributed to O–H and N–H bonds [13]. It should also be noted that the peaks observed in this range near 2900 and 3100 cm^{-1} correspond to the sp^3 - and sp^2 -hybridised C–H bonds [14]. The low-intensity 2133-cm^{-1} peak corresponds to C–N or N=C=N bonds [13, 15] formed either by the partial decomposition of $g\text{-C}_3\text{N}_4$ [13] or by incomplete polymerization of the precursor [15]. The range $1200\text{--}1600\text{ cm}^{-1}$ is commonly related to the characteristic vibration modes of C–N heterocycles [12]. It should be noted that, in the spectra of samples synthesized at 400°C and 450°C , we observe the 1095- and 2779-cm^{-1} peaks that are lacking in the spectra of the samples synthesized at higher temperatures. We conceive that these peaks correspond to thiocarbamide residues [16] in the synthesized material; these residues are removed from the material, as the temperature of synthesis is elevated.

In addition, we here mention the 885-cm^{-1} peak observed in the spectra of samples synthesized at temperatures of 500°C and higher. This peak is attributed to the formation of melam and melem, i.e., intermediate compounds formed upon the polymerization of carbon nitride [17].

Table 1. Position of maxima and the FWHM of PL bands of materials produced at different temperatures

Temperature of synthesis, °C	400	450	500	550	575	600	625
Position of the maximum, nm	417	453	456	468	490	494	494
FWHM, nm	78.3	66.3	69.6	94.9	126.3	132.4	130.3

All of the samples synthesized in the study exhibit intense PL. The PL spectra are shown in Fig. 4. As the temperature of synthesis of the material is elevated, the PL intensity decreases, reaches a minimum for the temperature 600°C, and slightly increases at 625°C. In addition, it should be noted that the PL band broadens, as the temperature is elevated to 500°C and higher.

The position of the maxima of the PL bands and their full width at half-maximum (FWHM) are listed in Table 1.

As the temperature of synthesis is increased from 400°C to 600°C, we observe a steady decrease in the PL intensity, with its slight increase for 625°C. At the same time, the position of the maximum shifts from 417 nm at a temperature of synthesis of 400°C to 494 nm at a temperatures of synthesis of 600°C and 625°C. The FWHM increases from 66.3 to 132.4 and 130.3 nm, as the temperature of synthesis is elevated from 450°C to 600°C and 625°C, respectively. This result is attributed to the complex structure of the PL band. Such a structure is formed because of the presence of two- and three-dimensional forms of $g\text{-C}_3\text{N}_4$ and an increase in the number of defects and impurities, whose levels lie at an energy of 0.2–0.5 eV below the bottom of the conduction band, during transformation of the material. Based on the systematic features established in the PL studies, we can recommend 450–500°C as the optimal temperature of synthesis for attainment of the best luminescence characteristics.

4. CONCLUSIONS

It is experimentally established that graphite-like carbon nitride is formed upon the heat treatment of thiocarbamide in the temperature range 400–625°C under conditions of limited access of an oxygen-containing atmosphere is established experimentally. According to the XRD data, the prevalent orientation of crystallites of the synthesized material corresponds to the [002] direction. FTIR spectroscopy study shows that, at the temperature of synthesis <500°C, the precursor is incompletely removed from the material, which is supported by observation of the 2779- and 1095-cm⁻¹ peaks. In the temperature range 500–625°C, the synthesized material exhibits close FTIR spectra, in which there is a peak attributed to the formation of melam and melem, i.e., intermediate com-

pounds formed upon the polymerization of carbon nitride. The presence of peaks related to sp^2 - and sp^3 -hybridized bonds suggests that there exists $g\text{-C}_3\text{N}_4$ in the two-dimensional form (sp^2 -hybridization) at the surface of the bulk material (sp^3 -hybridization).

The FTIR data show that there exist chemical bonds with oxygen in the material and provide some evidence of deviations of its composition from the stoichiometric ratio. This makes it possible to attribute the experimentally observed changes in the PL spectra to doping of the synthesized material with oxygen and to the formation of defects as a consequence of the decomposition of already synthesized $g\text{-C}_3\text{N}_4$ with increasing temperature. On the basis of systematic features established in the study, it is possible to recommend 450–500°C as the optimal temperature of synthesis for attainment of the best luminescence characteristics.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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