

Effect of the Graphitic Carbon Nitride Synthesis Atmosphere on Its Activity in the Photocatalytic Generation of Hydrogen Peroxide

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Abstract—Materials based on graphitic carbon nitride (g-C₃N₄) are intensely studied as promising photocatalysts of different reactions, hydrogen peroxide formation including. Effect of synthesis parameters of g-C₃N₄ obtained by thermolysis of melamine, urea, and thiourea on its composition and photocatalytic activity has been studied. The photocatalytic activity of obtained materials has been studied in the reaction of oxidative decomposition of organic dye and in oxygen reduction to form hydrogen peroxide. It has been shown that, in spite of incomplete polycondensation after thermolysis, the obtained samples display high values of photocatalytic activity. The work has shown that the photocatalytic activity of samples obtained at 550°C is by factor 2–4 higher than that for samples obtained at 500 and 600°C. It has been shown that the preparation of g-C₃N₄ from thiourea in air leads to photocatalyst with maximal activity, whereas melamine and urea produce the best catalyst under nitrogen atmosphere.

Keywords: graphitic carbon nitride, photocatalysis

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INTRODUCTION

Graphitic carbon nitride (g-C₃N₄) is a promising semiconducting material, which is intensely studied in recent time and can be used as efficient photocatalyst [1–5], electrocatalyst [6–8], material for light-emitting devices [9] and supercapacitors [10]. g-C₃N₄ meets many requirements for photocatalysts, namely: it is thermally and chemically stable [11, 12], has appropriate valence band and conduction band valley [13, 14], can be obtained from available compounds such as melamine, urea, thiourea, dicyandiamide [15, 16], and has small band gap that provides visible light absorption. Due to these properties, graphitic carbon nitride is considered as promising photocatalyst for water decomposition to form gaseous oxygen and hydrogen, CO₂ reduction, and oxidation of different organic contaminants.

Hydrogen peroxide generation is one of promising and intensely studied in recent time photocatalytic processes [17–20]. Hydrogen peroxide can be safely stored; it is an excellent environmentally benign oxidizing agent and is used in organic synthesis, biomedicine, and biosensorics [21–25]. Because of the absence of gaseous oxygen–hydrogen mixture on synthesis, the photocatalytic method of hydrogen perox-

ide production is potentially more advantageous and environmentally safe. Since photocatalytic formation of hydrogen peroxide is caused by oxygen reduction, required photocatalyst should have high reductive potential of photogenerated electrons. Graphitic carbon nitride may suit these requirements due to high position of conduction band and small energy gap width. In spite of high activity of graphitic carbon nitride materials in photocatalytic synthesis of hydrogen peroxide, the majority of works is devoted to photocatalysis on composite materials, whereas the effect of parameters of g-C₃N₄ synthesis on its properties is studied insufficiently.

The study of formation of graphitic carbon nitride showed that the polycondensation of urea and thiourea leads to production of g-C₃N₄ through formation of melamine followed by emergence of heptazine units and their subsequent coupling [15]. The composition and structure of final carbon nitride depends on completeness of heptazine units polycondensation, which is determined by synthesis conditions such as annealing temperature, duration, and atmosphere.

In the present work, we studied effect of certain parameters of synthesis of graphitic carbon nitride on

the activity of resultant photocatalyst in the production of hydrogen peroxide. Samples were obtained by thermolysis of urea, melamine, and thiourea in air and under nitrogen atmosphere in the temperature range of 500–600°C. Since the temperature range of g-C₃N₄ formation is close to its decomposition temperature (~650°C), special attention in the work was paid to assessment of yield of sample synthesis reactions, completeness of graphitic structure formation and concentration of functional groups on the surface. The obtained materials were studied in terms of composition and structure, while their photocatalytic activity was measured in both reactions of decomposition of model organic dye and the reactions of photocatalytic production of hydrogen peroxide in aqueous alcoholic solution.

EXPERIMENTAL

The samples of graphitic carbon nitride were obtained by the thermal decomposition of organic precursors with high nitrogen content (melamine, urea, and thiourea). A 5-g weighed sample of precursor was placed in a closed porcelain crucible and annealed at 500–600°C for 1–4 h in a muffle furnace in air or in a tube furnace in nitrogen flow. Heating rate in all experiments was 5 K/min. The obtained samples containing g-C₃N₄ were studied without further purification.

X-ray powder diffraction study was performed on a Rigaku D/MAX 2500 diffractometer with rotating anode (Japan) in reflection mode (Bragg–Brentano geometry) using CuK_{α1,2} radiation and graphite monochromator.

X-ray photoelectron spectra were registered on an ESCA facility of NanoPES Endstation at the Kurchatov synchrotron radiation source (Kurchatov Research Center) equipped with a SPECS Phoibos 150 high-resolution electron energy hemispherical analyzer with monochromatic X-ray radiation source (AlK_α, excitation energy of 1486.61 eV, Δ*E* = 0.2 eV) [26]. Studied powder samples were pressed into indium foil and attached to a manipulator.

IR spectra were recorded on a Bruker ALPHA Fourier-transform IR spectrometer (Germany) in the range of 400–4000 cm⁻¹ in frustrated total internal reflection mode. The content of carbon, hydrogen, and nitrogen was measured with a Carlo Erba Instruments EA 1108 CHN analyzer (Italy).

Specific surface area was measured by low-temperature nitrogen sorption at *T* = 77 K on a Quantachrome NOVA 4200e instrument (USA). Samples were preliminary degassed at 200°C in vacuum for 2 h. Obtained adsorption–desorption isotherms were used to determine specific surface area of samples by Brunauer–Emmett–Teller model.

To study kinetics of photocatalytic hydrogen peroxide formation, 0.2 mL of ethanol and 0.3 mL of 0.1 M

phosphate buffer solution was added to 2.5 mL of aqueous suspension of photocatalyst with concentration of 0.1 mg/mL. The suspension was exposed to irradiation of UV lamp (wavelength 366 nm) of CAMAG TLC Visualizer 2 instrument (Switzerland) with stirring. The concentration of evolved hydrogen peroxide was determined by the specific enzymatic reaction of 3,3',5,5'-tetramethylbenzidine (TMB) oxidation by horseradish peroxidase; for this purpose, 60-μL aliquots were taken each 5 min and added in a 96-well plate with a mixture of 204 μL of 0.1 M phosphate buffer, 6 μL of 5 × 10⁻⁵ M solution of horseradish peroxidase, and 30 μL of 10⁻³ M alcoholic TMB solution. The concentration of oxidized TMB was determined by spectrophotometry using a BMG Labtech SPECTROstar Nano spectrometer (Germany) with accuracy of ± 0.003 optical units.

The photocatalytic properties of obtained samples in the reaction of decomposition of methylene blue model dye were measured using previously described flow-type measurement installation [27, 28]. A dispersed weighed sample of photocatalyst was exposed to UV radiation using a 5.5-W high-pressure cylindrical mercury lamp immersed in reaction mixture. Methylene blue was used as a model dye at concentration of 25 mg/L. Continuous sampling was performed during experiment using a peristaltic pump, solution was passed through a U-shaped cuvette where optical absorption spectrum was measured each 3 s. The spectra were measured using a 500-W Ocean Optics HRX-2000 xenon lamp (USA) and an Ocean Optics QE65000 spectrophotometer.

RESULTS AND DISCUSSION

g-C₃N₄ samples were obtained in both air and under nitrogen atmosphere at 500–600°C. Increase in annealing duration and temperature led to decrease of yield for all precursors. The use of urea as precursor during annealing for 4 h at 600°C led to its complete decomposition in air, whereas thiourea under these conditions completely degraded in nitrogen. All obtained samples represent monophase carbon nitride with heptazine structure, typical XRD patterns of g-C₃N₄ are shown in Fig. 1a. X-ray powder diffraction (XRD) analysis for samples obtained from melamine displays peaks with smaller half-width probably due to increase in coherent-scattering regions and decrease of the number of defects in structure. When urea and thiourea were used as precursors, reflections on XRD pattern are considerably broadened, which indicates low structure ordering of obtained samples.

The IR spectra of obtained samples also confirm the formation of graphitic carbon nitride (Fig. 1b). The spectra of all samples exhibit vibrations of C=N bonds (1625 cm⁻¹), vibrations corresponding to heptazine (883 cm⁻¹) and triazine fragments (800 cm⁻¹), vibrations of aromatic rings (1550–1300 cm⁻¹) and

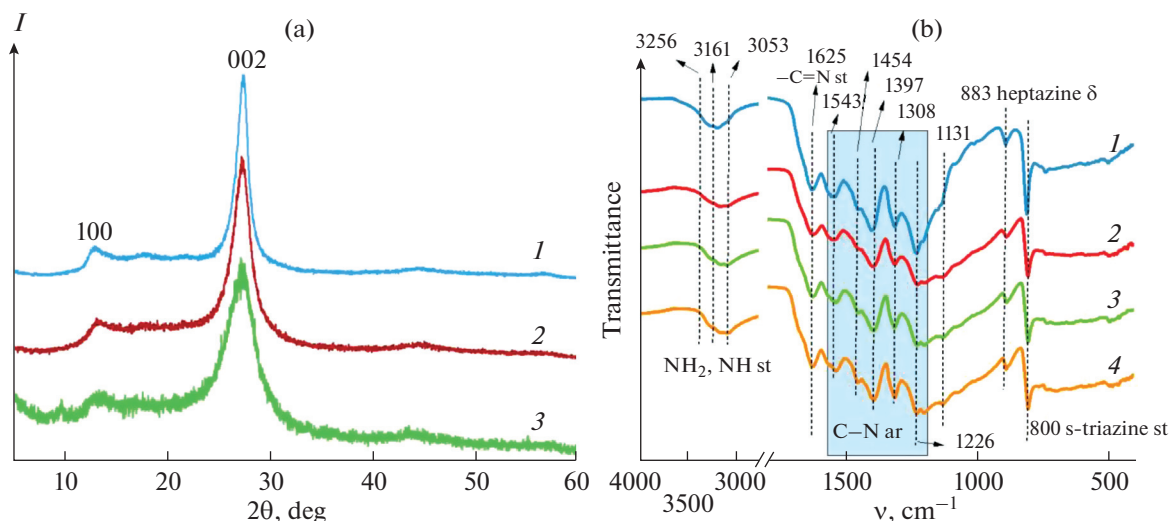


Fig. 1. (a) XRD patterns and (b) IR spectra of $g\text{-C}_3\text{N}_4$ samples obtained by the annealing of different precursors at 550°C for 1 h in air: (1) melamine, (2) thiourea, (3) urea, (4) melamine under nitrogen atmosphere.

residues of non-condensed intermediate products containing NH and NH_2 groups ($3300\text{--}3050\text{ cm}^{-1}$). The presence of amino groups indicates that polycondensation process is incomplete.

The results of CHN analysis (Table 1) indicate that obtained samples contain hydrogen, while the share of nitrogen is higher as compared with the nominal composition of $g\text{-C}_3\text{N}_4$ ($\text{N}/\text{C} = 1.33$) and lays in the range $1.35\text{--}1.46$. These N/C values and the results of IR spectroscopy indicate the presence of non-condensed fragments in the structure of $g\text{-C}_3\text{N}_4$ on thermolysis of organic precursors. Nonetheless, the composition is close to $\text{C}_6\text{N}_9\text{H}_4$ ($\text{N}/\text{C} = 1.5$) in the case of polycondensed one-dimensional chain of heptazine units, which is higher than the obtained by us values and indicates the presence of two-dimensional layers of carbon nitride with heptazine structure.

The incomplete joining of polycondensed heptazine chains into two-dimensional layers is also confirmed by X-ray photoelectron spectra (XPS) (Fig. 2, Table 2). So, XPS in the region of binding energy of C1s line shows the main peak corresponding to carbon in $g\text{-C}_3\text{N}_4$ structure, namely $\text{N}\text{--C}=\text{N}$ (289.3 eV) and the peaks of additional admixtures on the surface: $\text{C}\text{--C}$ (285.6 eV), $\text{C}\text{--OH}$ (287.2 eV), and $\text{O}\text{--C}=\text{O}$ (291 eV). XPS in the region of binding energy of N1s line displays the peaks corresponding to nitrogen atoms in graphitic carbon nitride: $\text{C}\text{--N}=\text{C}$ (399.7 eV) and $\text{N}\text{--}(\text{C}_3)$ (400.7 eV), as well as NH_x ($401\text{--}402\text{ eV}$) and $\text{N}\text{--O}$ ($402\text{--}403\text{ eV}$) corresponding to nitrogen in admixtures and functional groups of the surface. Thus, taking into account the results of CHN analysis, IR spectroscopy, and XPS, one can conclude that the obtained samples contain a considerable fraction of incompletely condensed heptazine layers.

The photocatalytic activity of obtained $g\text{-C}_3\text{N}_4$ samples was studied in the reaction of decomposition of methylene blue model dye and the photocatalytic reduction of oxygen dissolved in water–alcohol mixture into hydrogen peroxide. Since the positions of valence band and conduction band of carbon nitride have more negative potential as compared with oxide semiconductors, photoelectrons can participate in reduction reactions.

Figure 3 displays the values of reaction rate constants for photocatalytic formation of hydrogen peroxide in the presence of catalysts obtained by annealing in air and nitrogen for 4 h. In the case of $g\text{-C}_3\text{N}_4$ samples obtained by urea annealing, the large values of reaction rate constants are observed in the synthesis under nitrogen atmosphere. This fact may be caused by the lower stability of the obtained samples toward oxidation and further decomposition during synthesis, which is also confirmed by the low yields of $g\text{-C}_3\text{N}_4$ formation from urea in air as compared with nitrogen

Table 1. The results of CHN analysis of samples obtained by the annealing of different precursors at 550°C under nitrogen atmosphere for 4 h

Precursor	C	N	H	N/C
	at %			
Melamine	35	51	14	1.46
Urea	32	43	25	1.35
Thiourea	37	54	9	1.46

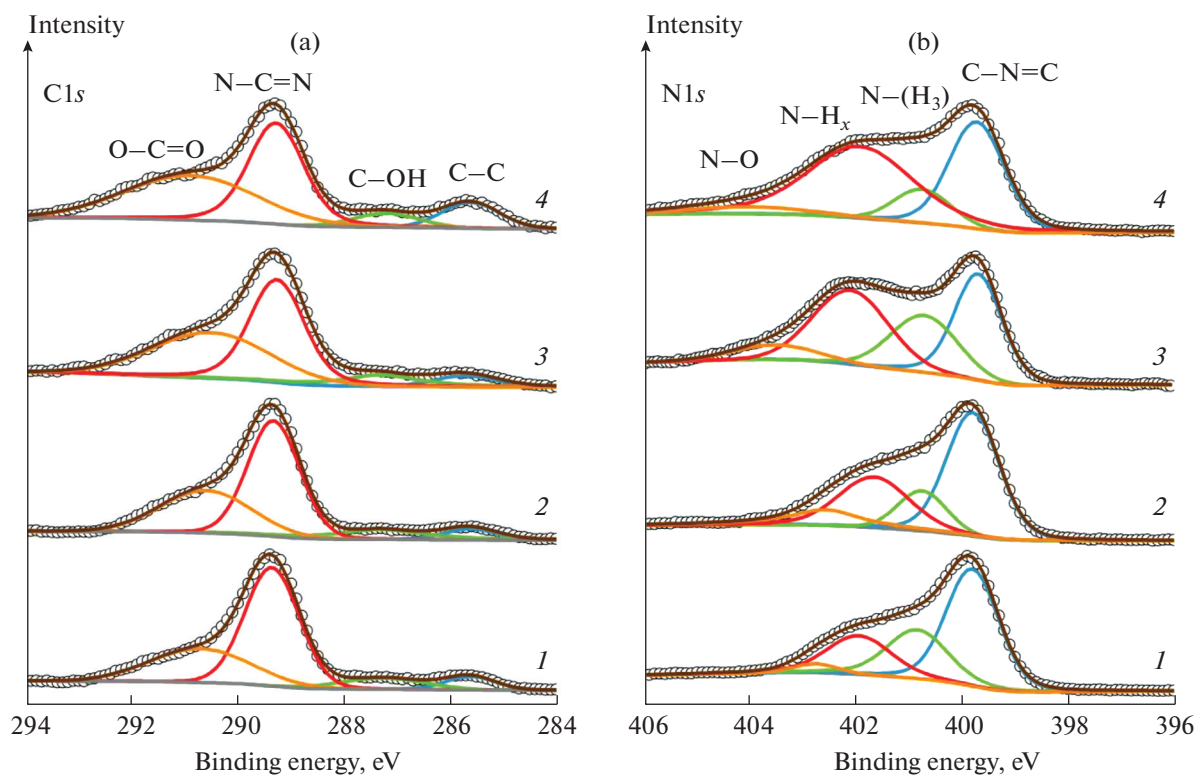


Fig. 2. X-ray photoelectron spectra of (a) C1s and (b) N1s lines of g-C₃N₄ samples obtained by annealing at 550°C for 1 h of (1) urea in air, (2) melamine under nitrogen atmosphere, (3) thiourea in air, (4) thiourea under nitrogen atmosphere.

atmosphere. The samples obtained from thiourea, on the contrary, show higher activity after synthesis under nitrogen atmosphere. The comparison of photoelectron spectra showed that g-C₃N₄ samples obtained from thiourea under nitrogen atmosphere contain much larger amino groups, which indicates lower polycondensation as compared with samples obtained from thiourea in air.

g-C₃N₄ samples obtained from melamine display lower values of H₂O₂ formation constants as compared with samples obtained from other precursors. In spite of higher crystallinity of samples obtained from melamine according to XRD, they have relatively low

activity, which can be explained by lower specific surface area. So, according to the data of low-temperature nitrogen adsorption, a g-C₃N₄ sample obtained by melamine thermolysis at 550°C for 4 h under nitrogen atmosphere has specific surface area of ~8 m²/g, whereas g-C₃N₄ samples obtained under similar conditions from urea and thiourea display these values of 26 and 23 m²/g, respectively.

The study of photocatalytic activity of obtained g-C₃N₄ samples in the reaction of decomposition of methylene blue model dye (Fig. 4) showed that samples obtained in nitrogen have higher values of decomposition constant.

Table 2. The results of quantitative analysis by XPS of g-C₃N₄ samples obtained by thermolysis of different precursors

Precursor, annealing atmosphere	Fraction of carbon atoms from XPS data, %				Fraction of nitrogen atoms from XPS data, %			
	O-C=O	N-C=N	C-OH	C-C	C-N=C	N-(C ₃)	N-H _x	N-O
Urea, air	29	56	8	6	49	14	27	11
Melamine, nitrogen	32	52	10	5	51	25	21	3
Thiourea, air	40	46	9	6	34	24	35	8
Thiourea, nitrogen	41	42	6	11	36	11	48	5

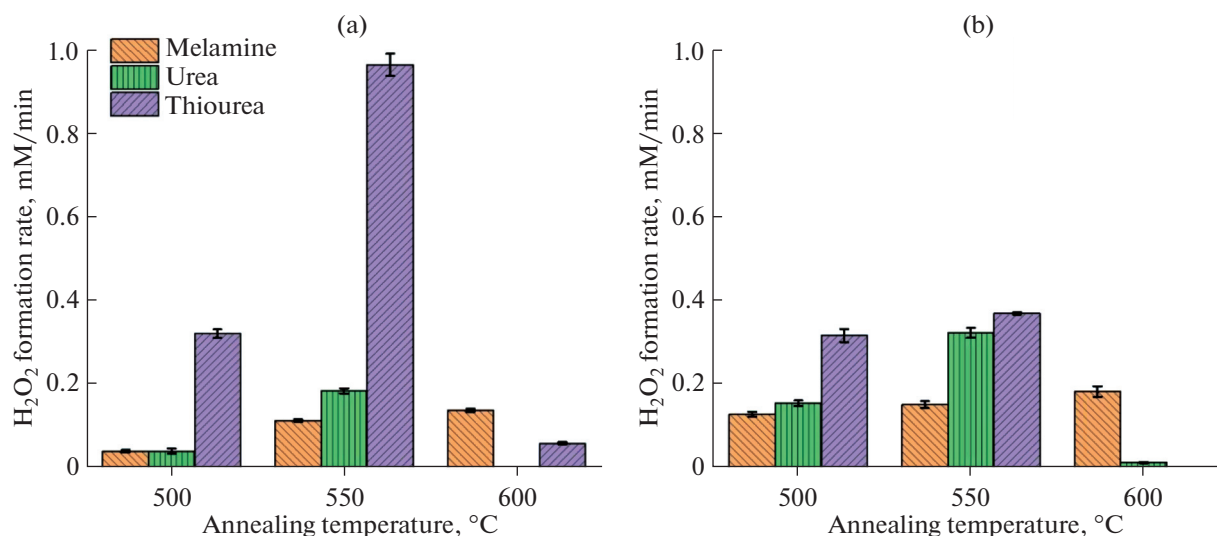


Fig. 3. Dependences of reaction rate constants for hydrogen peroxide formation on $g\text{-C}_3\text{N}_4$ synthesis temperature (a) in air and (b) under nitrogen atmosphere for 4 h.

CONCLUSIONS

We have studied the effect of parameters of graphitic carbon nitride synthesis from different precursors on its photocatalytic activity. The used synthesis conditions provide no complete polycondensation of graphitic structure: all obtained samples contain considerable fraction of amino groups on the surface. Nonetheless, the obtained samples display high photocatalytic activity in the reactions of hydrogen peroxide formation (up to 1 mM/min) and methylene blue decomposition ($1.8 \times 10^{-1} \text{ g}^{-1} \text{ s}^{-1}$), while the key parameters determining photocatalytic activity of $g\text{-C}_3\text{N}_4$

are temperature and atmosphere of synthesis. In the case of samples obtained from melamine and urea, products obtained under nitrogen atmosphere display higher activity, whereas the highest activity is observed for products obtained in air from thiourea as a precursor.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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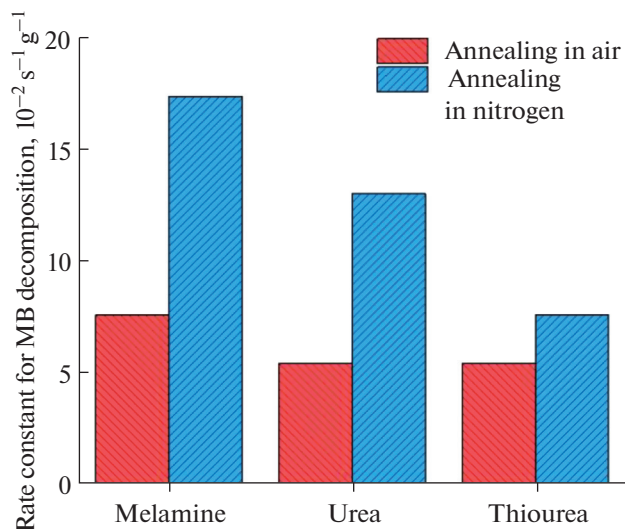


Fig. 4. Reaction rate constants for photocatalytic decomposition of methylene blue dye in the presence of $g\text{-C}_3\text{N}_4$ photocatalysts obtained by annealing in different atmosphere at 550°C for 1 h.

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