

M.E. Bondarenko, P.M. Silenko, Yu.M. Solonin, N.I. Gubareni,  
O.Yu. Khyzhun, N.Yu. Ostapovskaya

## SYNTHESIS O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> RUTILE COMPOSITE MATERIAL FOR PHOTOCATALYTIC APPLICATION

Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine  
3 Krzhizhanovsky Str., Kyiv, 03142, Ukraine, E-mail: mebondarenko@ukr.net

The development of novel materials ensuring the use of solar radiation as an inexhaustible source of renewable and environmentally friendly energy is one of the actual problems of materials science. Scientific research towards solving this important task showed the expediency of using photocatalytic processes with the participation of semiconductor systems. One of the most well-known catalyst titanium dioxide TiO<sub>2</sub> has photoactivity only in the ultraviolet region of the spectrum that significantly restricts its use. The application of based on undoped graphite-like carbon nitride g-C<sub>3</sub>N<sub>4</sub> or g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite catalysts allows using only part of the visible spectrum of solar radiation (with a wavelength of less than 460 nm). It is found that the doping of carbon nitride by oxygen significantly improves its photocatalytic properties to enhancing solar energy utilization. Therefore, to improve the photocatalytic activity of semiconductor photocatalyst, the coupling O-doped g-C<sub>3</sub>N<sub>4</sub> (O-g-C<sub>3</sub>N<sub>4</sub>) with rutile TiO<sub>2</sub> is a good strategy. Novel composite material O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> was synthesized by gas phase method of deposition of O-doped g-C<sub>3</sub>N<sub>4</sub> on particles of rutile powder under the special reactionary conditions of the pyrolysis of melamine. Obtaining O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> binary composite was confirmed through various analytical techniques including X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible diffuse reflectance spectra (UV-Vis-DRS) methods. It is found that the absorption spectra of the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> powders show a bathochromic shift of the long-wavelength edge of the fundamental absorption band (to 600 nm) relative to the absorption band of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (~ 460 nm). As a result, O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> photosensitivity is observed in the significant part of the visible region and the band gap of synthesized product is determined to be less than 2.4 eV versus 2.7 eV for undoped g-C<sub>3</sub>N<sub>4</sub> or g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>. One stage constructing heterojunction structure of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite may be used as a low-cost way to avoid the limitations of each component and realize a synergic effect in promoting the efficient generation and separation of charge carriers, thus boosting the photocatalytic activity to enhancing solar energy utilization.

**Keywords:** O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite, O-doped carbon nitride, rutile, photocatalyst, melamine, pyrolysis

### INTRODUCTION

Using sunlight by semiconductors for the production of renewable and clean energy and purification of water and air from toxic organic pollutants and pathogenic microflora is considered as a promising approach to address the imperative energy and environment problems [1–5]. By harvesting solar light to drive a series of important chemical reactions, semiconductor photocatalysis has emerged as one of the most fascinating technologies for wastewater treatment and converting low-density solar energy into high-density chemical energy.

Titanium dioxide (TiO<sub>2</sub>), as one of the most efficient metal oxide semiconductor photocatalyst, is widely used for many applications such as hydrogen evolution, CO<sub>2</sub> reduction and wastewater treatment because of its low cost, high chemical stability [1–4].

However, its photocatalytic activity is limited by rapid photogenerated electron-hole recombination and, most importantly, its wide band gap energy of ca. 3 eV (~ 3.2 and ~ 3.0 eV for anatase and rutile, respectively) which is activated only under ultraviolet (UV) light irradiation that accounts for about 5 % of solar light.

On the other hand, graphite-like carbon nitride g-C<sub>3</sub>N<sub>4</sub>, characterized as a non-toxic and chemically highly resistant material, has been shown to have huge potential as a promising photocatalyst capable of absorbing visible light for renewable energy (in particular, hydrogen production by photocatalytic water splitting) and for broad range of environmental applications (decomposition of organic pollutants and the destruction of pathogenic microflora). However, the application of based on pristine g-C<sub>3</sub>N<sub>4</sub> catalysts allows us using only part of the visible

spectrum of solar radiation (with a wavelength of less than 460 nm). Thus, in order to further enhance the light harvesting capability of g-C<sub>3</sub>N<sub>4</sub>, various bandgap engineering strategies, including doping by metal [6, 7] or non-metal atoms, in particular, oxygen [5, 8–12], are used. A number of researches have shown that the doping g-C<sub>3</sub>N<sub>4</sub> by oxygen to form O-g-C<sub>3</sub>N<sub>4</sub> significantly improved its photocatalytic properties [5, 8–17]. As a result, the absorption spectra of the O-doped carbon nitride powders show a bathochromic shift of the long-wavelength edge of the fundamental absorption band (to 498 nm or more) relative to the absorption band of pristine g-C<sub>3</sub>N<sub>4</sub> (~460 nm) [8, 9, 11, 12]. It is found that O-modified g-C<sub>3</sub>N<sub>4</sub> presented intrinsic electronic/band structure modulation [9], resulting in extended light absorption range for more effective visible-light utilization, up-shifted conduction band for stronger reducibility and more effective separation of photogenerated charge carriers, which are beneficial for improving photocatalytic hydrogen evolution activity. For example, according to [9], when using thermally oxidized porous g-C<sub>3</sub>N<sub>4</sub>, the 1430.1 μmol·g<sup>-1</sup>·h<sup>-1</sup> average photocatalytic hydrogen evolution is achieved in 8 h under visible-light irradiation, which was 4.3 times as high as that of the pristine g-C<sub>3</sub>N<sub>4</sub> sample (334.3 μmol·g<sup>-1</sup>·h<sup>-1</sup>). In report [10] is presented that O-doped material (O-g-C<sub>3</sub>N<sub>4</sub>) shows 6.1 and 3.1 times higher hydrogen evolution reaction activity (with apparent quantum efficiency of 7.8 % at 420 nm) than bulk and even 3D porous g-C<sub>3</sub>N<sub>4</sub>. According to investigation [13], the photocatalytic hydrogen evolution rate of O-doped g-C<sub>3</sub>N<sub>4</sub> was 13.9 times higher than that of bulk g-C<sub>3</sub>N<sub>4</sub>.

Oxygen doped carbon nitride was successfully applied for production hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which is widely used in wastewater treatment, pulp bleaching, pharmaceuticals *etc.* [12]. According to [12], oxygen doping g-C<sub>3</sub>N<sub>4</sub> changes the catalyst properties, leading to the promoted photocatalytic H<sub>2</sub>O<sub>2</sub> production capability in the absence of hole scavengers. As-prepared oxygen doped g-C<sub>3</sub>N<sub>4</sub> displays the H<sub>2</sub>O<sub>2</sub> concentration of 3.8 mmol·L<sup>-1</sup>, more than 7.6 times higher than that of neat g-C<sub>3</sub>N<sub>4</sub> [12].

Doping graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with oxygen contributes to the effectiveness of

the degradation of pollutants [14]. Thus, ozone treated carbon nitride increase photocatalytic rhodamine B (RhB) degradation constants by approximately 6 times [11], accelerates the photodegradation of methylene blue by a factor of 5 times and 2 times accelerates the generation of H<sub>2</sub> in comparison with untreated graphitic carbon nitride [4]. The 40 % metal-free oxygen doped porous graphitic carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) catalyst can degrade bisphenol A (15 mg·L<sup>-1</sup>) in 240 min with a mineralization rate as high as 56 % [15].

However, the known methods for oxygen-doped carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) producing suggest a two-stage process, since the synthesis involves post-treatment of the pre-synthesized undoped g-C<sub>3</sub>N<sub>4</sub> with ozone, nitric acid or hydrogen peroxide [8, 13, 15–17]. For example, long-term (10 h) heat treatment process (in a Teflon sealed autoclave at 140 °C) of the pre-synthesized g-C<sub>3</sub>N<sub>4</sub> by H<sub>2</sub>O<sub>2</sub> solution was used to obtain oxidized carbon nitride [8]. The pyrolysis method developed in Frantsevich Institute for Problems of Materials Science of NASU (IPM NASU) allows us to obtain oxygen-doped carbon nitride O-g-C<sub>3</sub>N<sub>4</sub> in one stage from melamine [18], urea [19–21] or cyanuric acid and urea mixture [22], and O-doped low-nitrogen containing carbon nitride O-C<sub>3</sub>N from pyridine [23, 24].

Besides the method of carbon nitride modification by oxygen, to increase the activity of the photocatalyst is also promising a different approach: creating g-C<sub>3</sub>N<sub>4</sub> based binary photocatalytic composite materials. For efficient light utilization, the fabrication and photocatalytic applications of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite materials have attracted much attention [1–4]. The synergistic effect of the combination of g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> leads to a significant improvement in the absorption of visible light and the effective separation of photo-generated electron-hole pairs. This greatly enhances the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite material, for example, for inactivating against bacteria in water under visible light.

However, both pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite exhibits photoactivity in the visible spectrum with limited utilization of solar energy (in the part of the visible diapason with wavelength below 460 nm only). While for modified by oxygen graphitic carbon nitride

samples (O-g-C<sub>3</sub>N<sub>4</sub>) synthesized in IPM [18–22] photosensitivity extends to a much larger region of the visible spectrum. It is found [8–11, 13, 15] that the doping of carbon nitride by oxygen significantly improves its photocatalytic properties to enhancing solar energy utilization. Thereby, to improve the photocatalytic activity of semiconductor photocatalyst, the coupling O-doped graphitic carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) with rutile TiO<sub>2</sub> is a good strategy. Therefore, the aim of the present was to obtain a nanocomposite based on O-doped carbon nitride and rutile phase of titanium dioxide (binary composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> rutile phase).

## EXPERIMENTAL

New composite material – O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (rutile phase) was synthesized in accordance with the one-step method developed in IPM for the synthesis of oxygen-doped carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) by gas phase method under the special reactionary conditions of the pyrolysis [25] of melamine [18], urea [19–21] or cyanuric acid and urea mixture [22]. Formation of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite was carried out under ambient pressure and pyrolysis-generated self-supporting atmosphere at the presence of a fixed volume of air. Nanoparticles of O-doped carbon nitride are formed in an vapor-gas reactionary space and are located by means of the deposition and the condensation on particles of rutile powder in more lower temperature (concerning the most highly temperature reaction zone) zones of reactionary space, far from a place of melamine precursor localization. The light yellow colored O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (rutile) was obtained by melamine heating with the rate not exceeding 10 deg·min<sup>-1</sup> and heat treatment at 550–580 °C for 1–1.5 h.

Deposition of O-g-C<sub>3</sub>N<sub>4</sub> (~ 6 % O) on the particles of rutile powder is confirmed through various analytical techniques including X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible diffuse reflectance spectra (UV-Vis-DRS) methods.

The powder X-ray diffraction (XRD) measurements were obtained from 5 to 80 ° of 2θ by a DRON-UM diffractometer with CuK<sub>α</sub>-radiation (λ = 0.154 nm) and nickel filter.

Fourier transform infrared spectroscopy (FTIR) in the reflectance mode was determined

between 450–4000 cm<sup>-1</sup> with the spectral resolution of 8 cm<sup>-1</sup> using a Nexus Nicolet FTIR spectrometer (Thermo Scientific) equipped with a Smart Collector reflectance accessory. Samples under investigation were prepared by pressing with KBr in 1:100 ratio.

X-ray photoelectronic spectra (XPS) of the samples were measured with a photoelectron spectrometer manufactured by SPECS Surface Nano Analysis Company (Germany). The system is equipped with a PHOIBOS 150 hemispherical analyzer. A base pressure of a sublimation ion-pumped chamber of the system was less than 5×10<sup>-10</sup> mbar during the present experiments. The Mg K<sub>α</sub> radiation (E = 1253.6 eV) was used as a source of XPS spectra excitation. The XPS spectra were measured at the constant pass energy of 25 eV. The energy scale of the spectrometer was calibrated by setting the measured Au4f<sub>7/2</sub> and Cu2p<sub>3/2</sub> binding energies to 84.00±0.05 and 932.66±0.05 eV, respectively, with regard to E<sub>F</sub>. For investigated sample, all the spectral features are attributed to the constituent element core-levels or Auger lines.

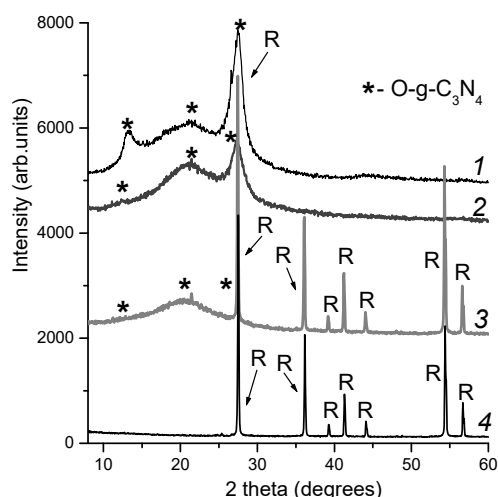
Diffuse reflectance spectra (DRS) of the powders were recorded in spectral diapason 200–1000 nm using a Perkin-Elmer Lambda Bio 35 UV-Vis with an integrating sphere Labsphere RSA-PR-20 with BaSO<sub>4</sub> as a scattering standard and converted into ultraviolet-visible (UV-Vis) absorption spectra by the Kubelka-Munk function [26].

## RESULTS AND DISCUSSION

At the heat treatment of melamine at 570 °C for 1.5 h in the most highly temperature reaction zone, in the placed in lower temperature zone the ceramic crucible with rutile powder, the light yellow colored powdery product are formed. The product obtained at 570 °C for 1 h has an even lighter shade. The obtained samples were denoted as O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h and O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h. To confirm the accordance of the obtained light yellow powder with the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composition, in the experiments the synthesized (IPM) O-doped carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) [18], pristine g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> (rutile phase) powdered samples also used. To understand the formation of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, the crystal structure of O-g-C<sub>3</sub>N<sub>4</sub>, pristine g-C<sub>3</sub>N<sub>4</sub>, rutile phase TiO<sub>2</sub> and presumably obtained O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite were firstly

investigated. Diffractograms of products O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h and O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h are practically identical. In the diffractograms of the both rutile titanium dioxide (Fig. 1, curve 4) and obtained light yellow powdered product O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h (Fig. 1, curve 3) there are strong peaks characteristic for the rutile phase (JCPDS No. 21-1276) with the most intense reflexes at  $2\theta = 27.4^\circ$  (110),  $36.2^\circ$  (101) and  $54.4^\circ$  (211). As is known, there are two characteristic reflexes at  $2\theta = 27.49^\circ$  (002) and  $12.40^\circ$  (100) in XRD patterns of pristine g-C<sub>3</sub>N<sub>4</sub> (Fig. 1, curve 1). These reflexes are caused by an interlayer stacking of aromatic heteroatomic rings with an interplane distance (0.324 nm) and the periodicity of stacking of heptazine fragments in one layer (0.714 nm). However, for O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> rutile composite sample (Fig. 1,

curve 3), one typical peak of both-g-C<sub>3</sub>N<sub>4</sub> and O-g-C<sub>3</sub>N<sub>4</sub> (002) is not clearly observed due to the coverage by that of rutile TiO<sub>2</sub> (110), while the absence of another peak at  $12.4^\circ$  of O-g-C<sub>3</sub>N<sub>4</sub> (Fig. 1, curve 2) is owing to its high dispersion on the surface of the composites. Occurrence of an additional reflex (wide halo) at  $2\theta = 21.45^\circ$  ( $d = 0.414$  nm) in the diffraction pattern of O-doped carbon nitride (O-g-C<sub>3</sub>N<sub>4</sub>) (Fig. 1, curve 2) is caused, as it was offered in [18, 19], with partial distortion of a planarity of its polymeric network  $((C_6N_7)-N)_n$  because of a dearomatization of some heterocycles at an oxidation. It is important to note that in the diffractogram of the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> binary composite a wide halo at  $21.45^\circ$  (characteristic for O-doped carbon nitride) is also clearly observed (Fig. 1, curve 3).



**Fig. 1.** X-ray diffraction spectra of: 1 – g-C<sub>3</sub>N<sub>4</sub>, 2 – O-g-C<sub>3</sub>N<sub>4</sub>, 3 – composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h, 4 – rutile TiO<sub>2</sub> samples

To stronger evidence the existence of O-g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> in the as-obtained sample, the surface chemistry of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h was analyzed by XPS analysis. Four elements (carbon, nitrogen, oxygen and titanium) can be identified in the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite sample in the survey scan XPS spectra (Fig. 2 a).

Under CVD conditions of the melamine precursor excess, the surface of the particles of rutile powder is almost completely covered with O-modified carbon nitride (according to XPS, the content of TiO<sub>2</sub> on the surface of the binary material is less than 10 %). This fact explains the weak intensity of the Ti peak on the survey spectrum. As one can see from the Fig. 2 b, the

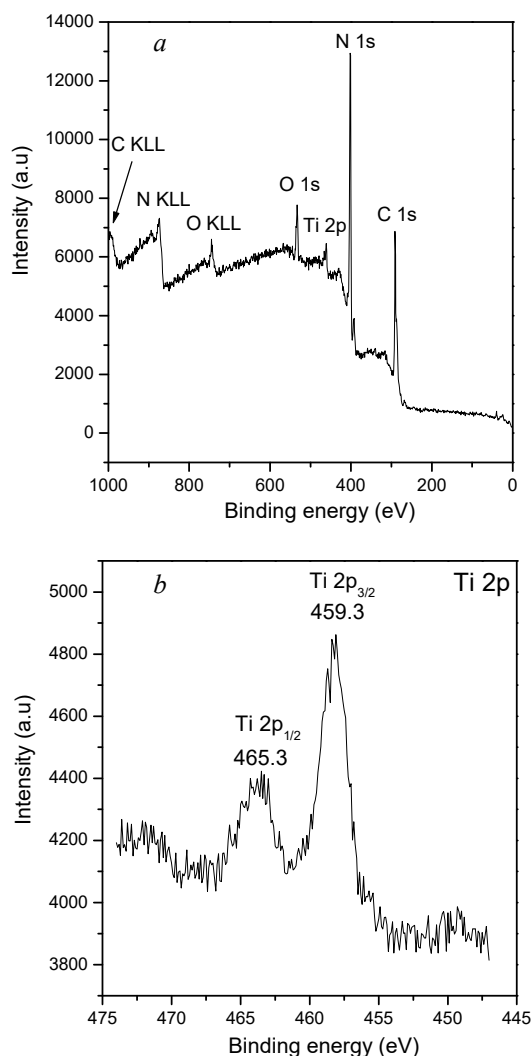
XPS Ti2*p* core-level spectrum recorded for this sample corresponds to that of titanium dioxide. As shown in the high-resolution Ti2*p* spectrum (Fig. 2 b), peaks at 458.8 and 464.5 eV are assigned to Ti2*p*<sub>3/2</sub>, and Ti2*p*<sub>1/2</sub> of TiO<sub>2</sub>.

In Fig. 3 a, the C1*s* spectra of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h could be deconvoluted into two main peaks centered at 284.6 and 288.0 eV. The major C1*s* peak at ~288 eV is identified as the tertiary carbon C-(N)<sub>3</sub> in the g-C<sub>3</sub>N<sub>4</sub> lattice. The weaker C1*s* 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 data [8, 16, 27]. Furthermore, the third weak peak at higher binding energy of

~290 eV was detected in O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h sample, which was accredited to C=O or C–O [8, 16, 17], suggesting the partial oxidation and formation of oxygen functional groups.

The deconvolution of the N1s spectrum (Fig. 3 b) of the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite

showed the presence of two main peaks centered at 398.5 and 399.8 eV, which were attributed to *sp*<sup>2</sup>-hybridized nitrogen (C=N–C) and tertiary *sp*<sup>3</sup>-hybridized nitrogen (N–(C)<sub>3</sub>) atoms in the carbon nitride network, respectively.



**Fig. 2.** XPS survey (a) and Ti2p core-level spectrum (b) for the composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h

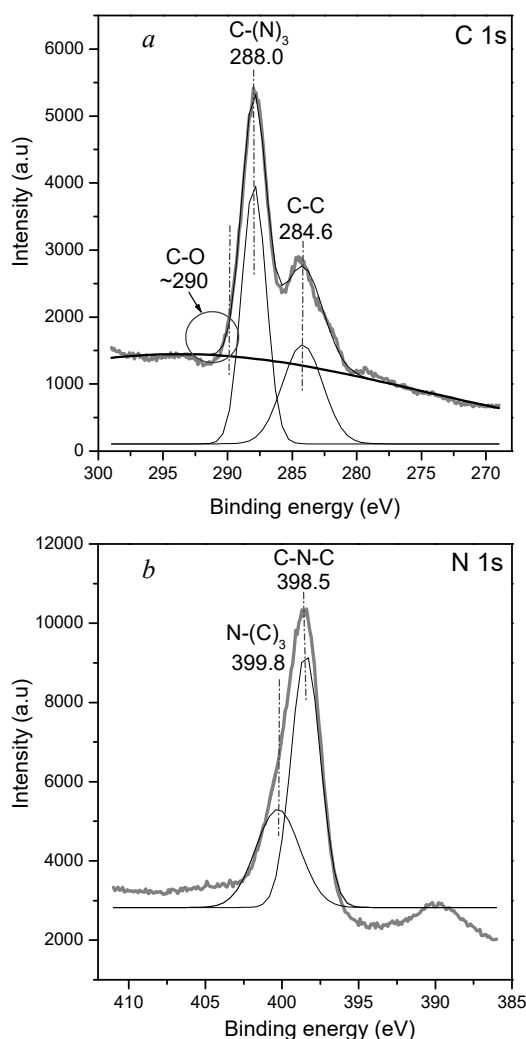
The deconvolution of the O1s spectrum of the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite showed the presence of two main maxima (Fig. 4). These peaks at binding energies about 531.5 and 529.4 eV in the high-resolution O1s XPS spectrum can be assigned to oxygen atoms in O-doped carbon nitride (C=O, C–O) and rutile (Ti–O), respectively. It is important to note that in the binary composite sample (O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>) the O1s signal intensity of oxygen-containing groups (C=O, C–O) is significantly stronger than

that of Ti–O. (In accordance with XPS results, the content of oxygen bound to carbon in the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h sample is 5.6 %).

Further demonstration of the formation of O-g-C<sub>3</sub>N<sub>4</sub> on rutile TiO<sub>2</sub> nanopowder surface is given by FTIR spectra (Fig. 5). IR spectra of all the samples (Fig. 5) contain, first of all, the peak near 810 cm<sup>-1</sup>, which could be ascribed to the characteristic out-of-plane bending mode of tri-s-triazine (heptazine) units in both g-C<sub>3</sub>N<sub>4</sub> and O-g-C<sub>3</sub>N<sub>4</sub> [18, 19]. Besides, in the IR spectra of

all samples there are several distinct intensive absorption bands in the 1200–1650 cm<sup>-1</sup> region, which also are characteristic for g-C<sub>3</sub>N<sub>4</sub> and

O-g-C<sub>3</sub>N<sub>4</sub> [18, 19] and correspond to the stretching vibrations of aromatic CN bonds in condensed nitrogen-carbon heterocycles.



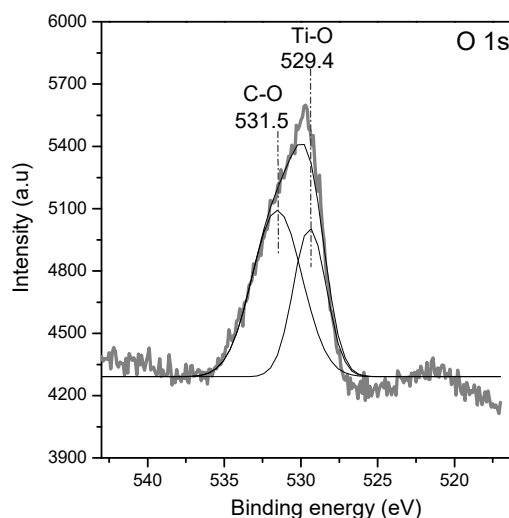
**Fig. 3.** High-resolution XPS C1s (a) and N1s (b) core-level spectra for the composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h

It should be noted that the IR spectrum of a sample O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h (Fig. 5, curve 2), which obtained with a shorter heat treatment time (1 h), is weakly structured. As one can see from the Fig. 5, curve 3, in the IR spectrum of obtained with a longer thermal treatment (for 1.5 h) sample O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h (which contains more than 5 % oxygen) there are absorption bands characteristic of heptazine fragments of the g-C<sub>3</sub>N<sub>4</sub> structure, as well as bands of the -OH, >C=O and -COOH groups, which are characteristic only for oxidized carbon nitride. The peak at 1089 cm<sup>-1</sup> is attributed to the stretching vibration of C-O, together with the

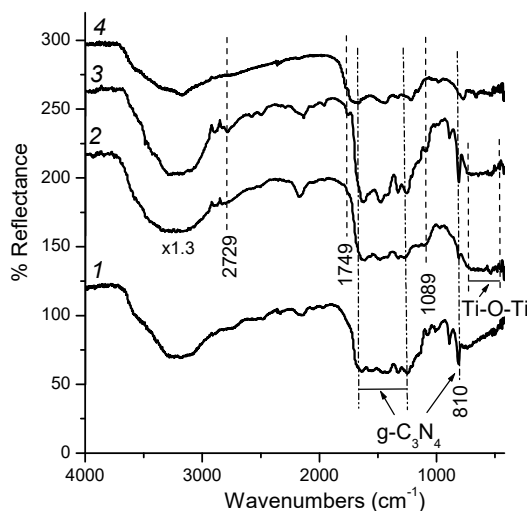
N-H and O-H signals around 3000–3600 cm<sup>-1</sup> generally related to the presence of hydroxyl groups. Most intensive signal becomes to emerge at ~1750 cm<sup>-1</sup>, which suggests the formation of carbonyl (carboxyl) groups. The presence of carboxyl groups is an evidence of a stretching band at ~2700 cm<sup>-1</sup>, characteristic for bond -O-H of carboxyl group. Note that the presence oxygen-containing functional groups which confirms the oxygen is doped into O-g-C<sub>3</sub>N<sub>4</sub> lattice, is in good agreement with the literature data [8, 12, 14, 16, 28]. However, some researchers believe (and provides convincing evidence also) that O doping preferentially

occurs at two-coordinated N position [10, 13, 15]. So, in [10] by experiment and DFT computation were identified that oxygen atoms preferentially replaced nitrogen atoms at two-coordinated N position. According to [10], after

Ar<sup>+</sup> etching to remove surface layer, O-g-C<sub>3</sub>N<sub>4</sub> sample still shows this lattice oxygen, confirming that O atoms are uniformly doped in the matrix.



**Fig. 4.** High-resolution XPS O1s core-level spectrum for the composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h



**Fig. 5.** IR spectra of: 1 – g-C<sub>3</sub>N<sub>4</sub>, 2 – composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h, 3 – composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h, 4 – O-g-C<sub>3</sub>N<sub>4</sub> samples

In attempt to obtain more evidence relative to the structure alternation due to the O doping, in [15] EPR was conducted to detect the spin state of unpaired electrons. The bulk g-C<sub>3</sub>N<sub>4</sub> exhibits one single Lorentzian line with a *g* factor of 2.003 due to the unpaired electron of the  $\pi$ -bonded aromatic rings [15]. It has been found [15] that in the EPR spectrum of O-doped carbon nitride a shoulder peak appears, probably because substituting the *sp*<sup>2</sup> N atom in the

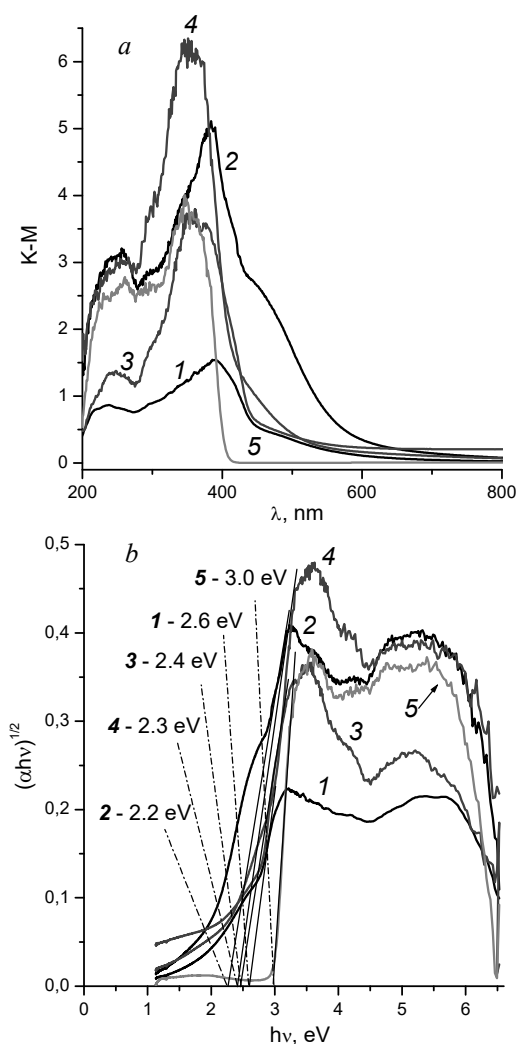
heptazine unit with an O atom creates one unpaired electron. Thus, oxygen position in O-modified carbon nitride network currently still under discussion. Probably in the structure of the O-g-C<sub>3</sub>N<sub>4</sub> lattice, both the addition of oxygen in the form of functional groups and the substitution of two-coordinated nitrogen with oxygen is possible. So, according to [13], the FTIR spectrum and XPS analysis of O1s and C1s verifies that doping O atoms either take the

place of two-coordinated nitrogen atoms or exist as hydroxide radicals linked to C atoms in the C=N-C ring.

For the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> samples, despite the strong light scattering of TiO<sub>2</sub> at low wavenumbers as well as the fact that the surface of the particles of rutile powder is almost completely covered with O-doped carbon nitride

(according to XPS), a weak wide signal near 800 cm<sup>-1</sup> was observed (Fig. 5, curves 2, 3).

UV-vis diffuse reflectance spectra (DRS) were used to study the light absorption properties of pure O-g-C<sub>3</sub>N<sub>4</sub> and O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> rutile composite compared to pristine rutile phase TiO<sub>2</sub> and undoped g-C<sub>3</sub>N<sub>4</sub> (Fig. 6 a).



**Fig. 6.** UV-Vis diffuse reflectance spectra of the powders converted by the Kubelka-Munk function (a) and estimation of band gap energies  $E_g$  (b) of: 1 – g-C<sub>3</sub>N<sub>4</sub>, 2 – O-g-C<sub>3</sub>N<sub>4</sub>, 3 – composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h, 4 – composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h, 5 – pure TiO<sub>2</sub> samples

The optical absorption spectra reveal that the pure undoped g-C<sub>3</sub>N<sub>4</sub> and rutile phase TiO<sub>2</sub> samples feature an intrinsic semiconductor-like absorption in the blue region of the visible spectrum and ultraviolet region respectively. There is a bathochromic shift of the absorption edge which expands to the significant part of the

visible light region for all synthesized powders doped with oxygen (from 460 nm for undoped g-C<sub>3</sub>N<sub>4</sub> to 600 nm with absorption trailing extended to more than 700 nm for O-g-C<sub>3</sub>N<sub>4</sub> in g-C<sub>3</sub>N<sub>4</sub> → O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h → O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h → O-g-C<sub>3</sub>N<sub>4</sub> range). It is assumed that in comparison with bulk g-C<sub>3</sub>N<sub>4</sub>, the absorption



band edge of O-g-C<sub>3</sub>N<sub>4</sub> is red shifted due to the presence of O-doping, and samples with more O-dopants show more obvious red shift [10]. The absorption band edge of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite is located between pure TiO<sub>2</sub> and oxygen modified O-C<sub>3</sub>N<sub>4</sub> samples, which further confirmed the electronic coupling of these two components in the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunction. Overall, the absorption intensity of all oxygen-doped samples (pure O-g-C<sub>3</sub>N<sub>4</sub>, O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h and especially O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h) is significant higher than that of pristine g-C<sub>3</sub>N<sub>4</sub> in the full spectrum and the absorption edges of oxygenated products are red shifted. It is assumed [13], that the red shift in the absorption wavelength indicates that the introduction of oxygen results in the absorption of more light energy to produce more photogenerated electron-hole pairs, which contribute to the improvement in the photoactivity of the catalysts. The band gap energies of the materials were estimated by the Kubelka–Munk equation by transforming the spectra into  $(ah\nu)^{1/2}$  versus  $h\nu$  (for g-C<sub>3</sub>N<sub>4</sub>, the  $n$  is  $\frac{1}{2}$  for the indirect band gap semiconductor). The band gap energy ( $E_g$ ) estimated from the

intercept of the tangents to the plots of  $(ah\nu)^{1/2}$  vs photon energy decreases in the range O-g-C<sub>3</sub>N<sub>4</sub> < O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1.5h < O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-1h < g-C<sub>3</sub>N<sub>4</sub> < TiO<sub>2</sub> (rutile phase) and has values of 2.2, 2.3, 2.4, 2.6, and 3.0 eV, respectively, as shown in the Fig. 6 b. The obtained data confirm that the construction of heterojunction structure can be responsible for the overall improvement of light adsorption intensity and show the possibility of practical use of oxygen-doped O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite in photocatalysis.

## CONCLUSIONS

Novel composite material O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> rutile with photoactivity in significant part of visible light spectral diapason was obtained. Thus, the integration of two favorable characteristics (heteroatom introducing and the construction of heterojunction structure) in the novel composite O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (rutile phase) may be used as a cost-effective way to avoid the drawbacks of each component and realize a synergic effect in promoting the efficiently transfer of photo-generated electron-hole pairs to restrict the recombination, thus boosting the photocatalytic activity.

## Синтез композитного матеріалу O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> рутил для фотокаталітичного застосування

М.Е. Бондаренко, П.М. Силенко, Ю.М. Солонін, Н.І. Губарені, О.Ю. Хижун, Н.Ю. Остаповська

*Інститут проблем матеріалознавства ім. І.М. Францевича Національної академії наук України  
вул. Кржижановського, 3, Київ, 03142, Україна, tebondarenko@ukr.net*

Створення сучасних матеріалів, що забезпечують використання сонячного випромінювання як невичерпного джерела відновлюваної і екологічно чистої енергії – одне з найбільш актуальних завдань матеріалознавства. Наукові дослідження в напрямку вирішення цього важливого завдання показали доцільність використання фотокаталітичних процесів за участю напівпровідникових систем. Один з найбільш відомих каталізаторів діоксид титану TiO<sub>2</sub> має фотоактивність тільки в ультрафіолетовій області спектра, що істотно обмежує його використання. Застосування каталізатора на основі недопованого графітоподібного нітриду вуглецю g-C<sub>3</sub>N<sub>4</sub> або композиту g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> дозволяє використовувати тільки частину видимого спектру сонячного випромінювання (з довжиною хвилі менше 460 нм). Встановлено, що допування нітриду вуглецю киснем значно покращує його фотокаталітичні властивості. Таким чином, для підвищення фотокаталітичної активності напівпровідникового фотокаталізатора хорошою стратегією є поєднання O-допованого g-C<sub>3</sub>N<sub>4</sub> (O-g-C<sub>3</sub>N<sub>4</sub>) з рутилом TiO<sub>2</sub>. Новий композитний матеріал O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> був синтезований газофазним методом за допомогою осаження O-допованого g-C<sub>3</sub>N<sub>4</sub> на частинці порошку рутилу в особливих реакційних умовах піролізу меламіну. Отримання бінарного композиту O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> було підтверджено різними аналітичними методами, включаючи рентгенівську порошкову дифракцію, інфрачервону спектроскопію з Фур'є-перетворенням, рентгенівську фотоелектронну спектроскопію і спектри дифузного відбиття в ультрафіолетовому та видимому діапазонах. Встановлено, що в спектрах поглинання порошків

O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> спостерігається батохромний зсув довгохвильового краю смуги фундаментального поглинання (до 600 нм) відносно смуги поглинання g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (~ 460 нм). В результаті фоточутливість O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> спостерігається в значній частині видимої області спектра, а ширина забороненої зони синтезованого продукту становить менше 2.4 eV проти 2.7 eV для недопованого g-C<sub>3</sub>N<sub>4</sub> або g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>. Одностадійний метод створення гетероперехідної структури – композиту O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> може бути використаний як економічно вигідний спосіб уникнути недоліків кожного компонента і реалізувати синергетичний ефект в сприянні генерації і розподілу носіїв заряду, таким чином посилюючи фотокаталітичну активність матеріалу для більш ефективного використання сонячної енергії.

**Ключові слова:** композит O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, O-допований нітрид вуглецю, рутил, фотокаталізатор, меламін, піроліз

## Синтез композитного матеріала O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> рутил для фотокаталітичного застосування

М.Э. Бондаренко, П.М. Силенко, Ю.М. Солонин, Н.И. Губарени, О.Ю. Хижун, Н.Ю. Остаповская

Институт проблем материаловедения им. И.Н. Францевича Национальной академии наук Украины  
ул. Кржижановского, 3, Киев, 03142, Украина, tebondarenko@ukr.net

Создание современных материалов, обеспечивающих использование солнечного излучения в качестве неисчерпаемого источника возобновляемой и экологически чистой энергии – одна из наиболее актуальных задач материаловедения. Научные исследования в направлении решения этой важной задачи показали целесообразность использования фотокаталитических процессов с участием полупроводниковых систем. Один из наиболее известных катализаторов диоксид титана TiO<sub>2</sub> обладает фотоактивностью только в ультрафиолетовой области спектра, что существенно ограничивает его использование. Применение катализатора на основе недопированного графитоподобного нитрида углерода g-C<sub>3</sub>N<sub>4</sub> или композита g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> позволяет использовать только часть видимого спектра солнечного излучения (с длиной волны менее 460 нм.) Установлено, что допирование нитрида углерода кислородом значительно улучшает его фотокаталитические свойства. Таким образом, для повышения фотокаталитической активности полупроводникового фотокаталитизатора хорошей стратегией является сочетание O-допированного g-C<sub>3</sub>N<sub>4</sub> (O-g-C<sub>3</sub>N<sub>4</sub>) с рутилом TiO<sub>2</sub>. Новый композитный материал O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> был синтезирован газофазным методом посредством осаждения O-допированного g-C<sub>3</sub>N<sub>4</sub> на частицы порошка рутила в особых реакционных условиях пиролиза меламин. Получение бинарного композита O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> было подтверждено различными аналитическими методами, включая рентгеновскую порошковую дифракцию, инфракрасную спектроскопию с Фурье-преобразованием, рентгеновскую фотоэлектронную спектроскопию и спектры диффузного отражения в ультрафиолетовом и видимом диапазонах. Установлено, что в спектрах поглощения порошков O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> наблюдается батохромный сдвиг длинноволнового края полосы фундаментального поглощения (до 600 нм) относительно полосы поглощения g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (~ 460 нм). В результате фоточувствительность O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> наблюдается в значительной части видимой области спектра, а ширина запрещенной зоны синтезированного продукта составляет менее 2.4 эВ против 2.7 эВ для недопированного g-C<sub>3</sub>N<sub>4</sub> или g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>. Одностадийный метод создания гетеропереходной структуры – композита O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> может быть использован как экономически выгодный способ избежать недостатков каждого компонента и реализовать синергетический эффект в содействии генерации и разделению носителей заряда, таким образом усиливая фотокаталитическую активность материала для более эффективного использования солнечной энергии.

**Ключевые слова:** O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, O-допированный нитрид углерода, рутил, фотокаталізатор, меламін, піроліз

## REFERENCES

- Zhong R., Zhang Z., Luo S., Zhang Z.C., Huang L., Gu M. Comparison of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> 2D/2D nanocomposites from three synthesis protocols for visible-light induced hydrogen evolution. *Catal. Sci. Technol.* 2019. **9**(1): 75.
- Lei J., Chen B., Lv W., Zhou L., Wang L., Liu Y., Zhang J. Inverse opal TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite with heterojunction construction for enhanced visible light-driven photocatalytic activity. *Dalton Trans.* 2019. **48**(10): 3486.
- Chen X., Wei J., Hou R., Liang Y., Xie Z., Zhu Y., Zhang X., Wang H. Growth of g-C<sub>3</sub>N<sub>4</sub> on mesoporous TiO<sub>2</sub> spheres with high photocatalytic activity under visible light irradiation. *Appl. Catal., B.* 2016. **188**: 342.
- Li H., Wu X., Yin S., Katsumata K., Wang Y. Effect of rutile TiO<sub>2</sub> on the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>/brookite-TiO<sub>2-x</sub>N<sub>y</sub> photocatalyst for NO decomposition. *Appl. Surf. Sci.* 2017. **392**: 531.
- Wen J., Xie J., Chen X., Li X. A review on g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts. *Appl. Surf. Sci.* 2017. **391**: 72.
- Grodzyuk G.Ya., Shvalagin V.V., Andryushina N.S., Panasiuk Ya.V., Korzhak G.V., Kuchmy S.Ya., Skoryk N.A. Carbon nitride nanocomposites with layered niobates as photocatalysts for hydrogen evolution from aqueous solutions of organic acids by the action of visible light. *Theor. Exp. Chem.* 2018. **54**(2): 99.
- Andryushina N., Shvalagin V., Korzhak G., Grodzyuk G., Kuchmy S., Skoryk M. Photocatalytic evolution of H<sub>2</sub> from aqueous solutions of two-component electron-donor substrates in the presence of g-C<sub>3</sub>N<sub>4</sub> activated by heat treatment in the KCl + LiCl melt. *Appl. Surf. Sci.* 2019. **475**: 348.
- Li J., Shen B., Hong Z. A facile approach to synthesize novel oxygen-doped g-C<sub>3</sub>N<sub>4</sub> with superior visible-light photoreactivity. *Chem. Commun.* 2012. **48**(98): 12017.
- Yang L.Q., Huang J.F., Shi L., Cao L.Y., Yu Q., Jie Y.N., Fei J., Ouyang H.B., Ye J.H. A surface modification resultant thermally oxidized porous g-C<sub>3</sub>N<sub>4</sub> with enhanced photocatalytic hydrogen production. *Appl. Catal. B.* 2017. **204**: 335.
- Huang Z.F., Song J., Pan L., Wang Z., Zhang X., Zou J.J. Carbon nitride with simultaneous porous network and O-doping for efficient solar-energy-driven hydrogen evolution. *Nano Energy.* 2015. **12**: 646.
- Qu X., Hu S., Bai J., Li P., Lu G., Kang X. A facile approach to synthesize oxygen doped g-C<sub>3</sub>N<sub>4</sub> with enhanced visible light activity under anoxic conditions via oxygen-plasma treatment. *New J. Chem.* 2018. **42**(7): 4998.
- Wang H., Guan Y., Hu S., Pei Y., Ma W., Fan Z. Hydrothermal synthesis of band gap-tunable oxygen doped g-C<sub>3</sub>N<sub>4</sub> with outstanding "two channel" photocatalytic H<sub>2</sub>O<sub>2</sub> production ability assisted by dissolution-precipitation process. *Nano.* 2019. **14**(02): 1950023.
- Wang C., Fan H., Ren X., Ma J., Fang J., Wang W. Hydrothermally induced oxygen doping of graphitic carbon nitride with a highly ordered architecture and enhanced photocatalytic activity. *Chem. Sus. Chem.* 2018. **11**(4): 700.
- Liu S., Li D., Sun H. Ang H.M., Tade M.O., Wang S. Oxygen functional groups in graphitic carbon nitride for enhanced photocatalysis. *J. Colloid Interface Sci.* 2016. **468**: 176.
- Qiu P.X., Xu C.M., Chen H., Fang J., Xin W., Ruifeng L., Xirui Z. One step synthesis of oxygen doped porous graphitic carbon nitride with remarkable improvement of photo-oxidation activity: Role of oxygen on visible light photocatalytic activity. *Appl. Catal. B.* 2017. **206**: 319.
- Ming L., Yue H., Xu L., Chen F. Hydrothermal synthesis of oxidized g-C<sub>3</sub>N<sub>4</sub> and its regulation of photocatalytic activity. *J. Mater. Chem. A.* 2014. **2**(45): 19145.
- Liu X., Ji H., Wang J., Xiao J., Yuan H., Xiao D. Ozone treatment of graphitic carbon nitride with enhanced photocatalytic activity under visible light irradiation. *J. Colloid Interface Sci.* 2017. **505**: 919.
- Kharlamov A., Bondarenko M., Kharlamova G. Method for the synthesis of water-soluble oxide of graphite-like carbon nitride. *Diamond Relat. Mater.* 2016. **61**: 46.
- Kharlamov A., Bondarenko M., Kharlamova G., Gubareni N. Features of the synthesis of carbon nitride oxide (g-C<sub>3</sub>N<sub>4</sub>)O at urea pyrolysis. *Diamond Relat. Mater.* 2016. **66**: 16.
- Kharlamov A., Bondarenko M., Kharlamova G., Fomenko V. Synthesis of reduced carbon nitride at the reduction by hydroquinone of water-soluble carbon nitride oxide (g-C<sub>3</sub>N<sub>4</sub>)O. *J. Solid State Chem.* 2016. **241**: 115.
- Kharlamov O., Bondarenko M., Kharlamova G., Silenko P., Khyzhun O., Gubareni N. Carbon Nitride Oxide (g-C<sub>3</sub>N<sub>4</sub>)O and Heteroatomic N-graphene (Azagraphene) as Perspective New Materials in CBRN defense. In: *Nanostructured Materials for the Detection of CBRN, NATO Science for Peace and Security Series A: Chemistry and Biolog.* (J. Bonca, S. Kruchinin Eds., Springer, Dordrecht, Chapter, V. 20. 2018). P. 245.
- Bondarenko M., Silenko P., Gubareni N., Khyzhun O., Ostapovskaya N., Solonin Yu. Synthesis of multilayer azagraphene and carbon nitride oxide. *Him. Fiz. Tehnol. Poverhni.* 2018. **9**(4): 393.

23. Kharlamov O., Bondarenko M., Kharlamova G. O-Doped Carbon Nitride (O-g-C<sub>3</sub>N) With High Oxygen Content (11.1 mass. %) Synthesized by Pyrolysis of Pyridine. In: *Nanotechnology to Aid Chemical and Biological Defense, NATO Science for Peace and Security Series A: Chemistry and Biology*. V. 9. (Dordrecht: Springer Science+Business Media, 2015). P. 129.
24. Kharlamov A.I., Bondarenko M.E., Kharlamova G.A. New method for synthesis of oxygen-doped graphite-like carbon nitride from pyridine. *Russ. J. Appl. Chem.* 2014. **87**(9): 1284.
25. Kharlamov A.I., Bondarenko M.E., Kirillova N.V. New method for synthesis of fullerenes and fullerene hydrides from benzene. *Russ. J. Appl. Chem.* 2012. **85**(2): 233.
26. Kelyp O.O., Petrik I.S., Vorobets V.S., Smirnova N.P., Kolbasov G.Ya. Sol-gel synthesis and characterization of mesoporous TiO<sub>2</sub> modified with transition metal ions (Co, Ni, Mn, Cu). *Him. Fiz. Tehnol. Poverhni.* 2013. **4**(1): 105.
27. Dong F., Zhao Z., Xiong T., Ni Z., Zhang W., Sun Y., Ho W.K. In situ construction of g-C<sub>3</sub>N<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> metal-free heterojunction for enhanced visible-light photocatalysis. *ACS Appl. Mater Interfaces.* 2013. **5**(21): 11392.
28. Wang P., Guo X., Rao L., Wang C., Guo Y., Zhang L. A weak-light-responsive TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite film: photocatalytic activity under low-intensity light irradiation. *Environ. Sci. Pollut. Res.* 2018. **25**(20): 20206.

Received 29.07.2019, accepted 20.11.2019