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SYNTHESIS AND CATALYTIC PROPERTIES OF NITROGEN-CONTAINING CARBON NANOTUBES

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Nitrogen-containing carbon nanotubes (CNTs) were synthesized by the CVD method on oxide catalysts of Al-Fe-Mo-O by adding acetonitrile or ethylenediamine to the carbon source (propylene), or completely replacing it, as well as impregnating the original CNTs with urea, followed by heat treatment. The structure of nitrogen-containing CNTs (N-CNT) was characterized by the method of Raman scattering, transmission electron microscopy (TEM), differential thermal and gravimetric analysis (DTA, DTG) and X-ray photoelectron spectroscopy (XPS). The influence of the synthesis method on the number and chemical state of nitrogen heteroatoms in the structure of the carbon matrix is found. According to the TEM, nitrogen-containing CNTs have a characteristic bamboo-like structure, which is less perfect compared to the structure of the original CNTs: the characteristic Raman bands (G and D) are shifted to higher frequencies, their half-width and band D intensity increase relative to G. This is also manifested in the lower thermal stability of nitrogen-containing CNTs. According to the XPS, the direct synthesis of nitrogen-containing CNTs increases the total content of nitrogen atoms and the proportion of pyrrolic and quaternary nitrogen against the background of a significant decrease in the amount of pyridinic form. This can be explained by the fact that nitrogen is evenly distributed throughout the carbon matrix of CNTs, and during nitriding of CNTs with urea, nitrogen is included mainly in the surface layers and defects, because the pyridine form is characteristic of the edge location of the nitrogen atom in the graphene plane. The catalytic effect of multilayer nitrogen-containing carbon nanotubes (N-CNT) on the kinetics of decomposition of hydrogen peroxide in aqueous solutions at different pH values is considered. It is concluded that the method of direct synthesis of nitrogen-containing CNTs allows to obtain more catalytically active carbon nanotubes containing more nitrogen, mainly pyrrolic and quaternary type. It has been found that regardless of the method of synthesis, the maximum catalytic activity in the decomposition of hydrogen peroxide is observed at pH 7.

Keywords: nitrogen-containing carbon nanotubes, catalysis, hydrogen peroxide

INTRODUCTION

Carbonaceous materials have been popular for the oxygen reduction reaction, in particular in the developing catalytic systems. Carbon nanotubes (CNTs) attract more and more attention due to their outstanding mechanical, physical and chemical properties. As it is known, CNTs are found to show catalytic properties. Additional treatment, namely functionalization and doping with heteroatoms, modifies the CNTs electronic system, facilitates the electron transfer and in this way increases the oxygen electro-reduction reaction [1–3]. Oxidation is the most common method of chemical modification of CNTs. As a result of such treatment, different oxygen content groups are formed on the surface of CNTs. Most often carboxyl, hydroxyl, carbonyl and lactone groups are observed on the

surface of oxidized CNTs. In order to accelerate the activity and the stability against degradation, the introducing of nitrogen, sulfur, boron or phosphorus atoms to the nanotubes structure was proposed [4, 5]. As a rule, the nitrogen doping is carried out by using two methods. The first one is the CNTs doping during their synthesis by arc or chemical vapor deposition. The second one is the doping of pre-synthesized CNTs through their treatment by nitrogen-enriched precursors (urea, melamine, pyridine, ammonia, etc.) [6–8].

Nitrogen atoms are similar to carbon ones by size, consequently, such atoms successfully replace the carbon ones in crystal lattice [6, 9]. The π -electrons of the carbon atoms conjugate with the unshared electron pair of the of nitrogen atom [8, 9], which is built-in to the carbon lattice. In this case, nitrogen exhibits properties of an electron donor in relation to carbonaceous

material [10]. Nitrogen on the surface of carbon material is represented by a variety of forms (pyridine, pyrrole *etc.*) [6–12].

At least three types of nitrogen are found in CNTs. These are pyridinic nitrogen, pyrrolic nitrogen and quaternary nitrogen. The pyridinic N-type is an sp^2 hybridized nitrogen atom located at the edges or at defects of the graphene sheets (Fig. 1 *a*). These pyridinic nitrogen atoms have a localized electron lone pair which are active in

base catalyzed reactions. Therefore, the optimization of the amount of pyridinic nitrogen is important for catalysis. The pyrrolic N-type is sp^3 hybridized and part of a five membered ring structure (Fig. 1 *b*). The quaternary N is a carbon substituted nitrogen atom located in the graphene sheet (Fig. 1 *c*). A fourth type has been reported and labeled as N–X species (Fig. 1 *d*), believed to be an oxidized type of pyridinic N.

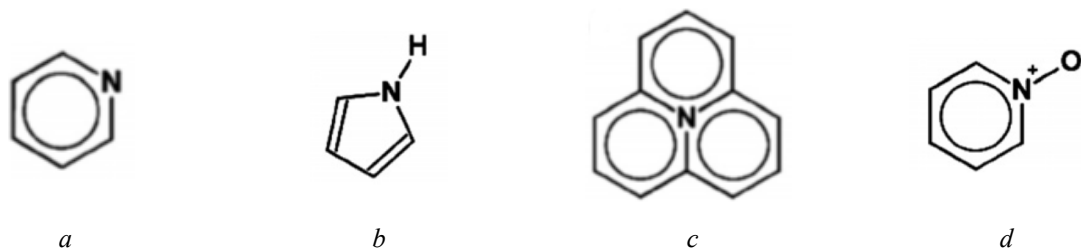


Fig. 1. Types of nitrogen species found in N-CNTs: *a* – pyridinic, *b* – pyrrolic, *c* – quaternary, *d* – N-oxide

Although the different types of nitrogen present in the CNT's have been described, mainly the increase of the amount of nitrogen incorporated has been the focus in many studies [6, 12].

The aim of this work is to synthesize nitrogen-containing CNTs by different methods, to characterize them, and to study the catalytic properties of N-CNTs characterized by a high specific surface area, the main part of which is the outer surface of the tubes, which significantly reduces the effect of diffusion on catalytic reactions and contains nitrogen atoms.

RESULTS AND DISCUSSIONS

Methods and materials. CNTs were synthesized by catalytic vapor deposition according to the technique we developed earlier [13, 14], conformed to the requirements of the standard TU U 24.1-03291669-009:2009 Carbon Nanotubes Chuiko Institute of Surface Chemistry, NAS of Ukraine. N-CNT's were obtained by a similar method by precipitating them from the gas phase using 100 % acetonitrile and mixture of ethylenediamine (20 %) + propylene at the temperature of 750 °C (which is 100 °C higher than in the synthesis of pure carbon CNTs) on an Al-Fe-Mo-O catalyst. A possible growth scheme for nitrogen-doped CNTs is shown in Fig. 2 [15].

Figs. 3, 4 present TEM images (transmission electron microscope JEM-100CXII, accelerating

voltage – 100 kV, resolution reaches 2.04 Å) of product obtained from 100 % acetonitrile and of product obtained from 100 % ethylenediamine.

As can be seen from the presented images (Figs. 3, 4), the obtained structures have a bamboo-like appearance, characteristic of nitrogen-containing nanotubes [16–18].

One sample of nitrogen-containing CNTs was synthesized from pure carbon CNTs by oxidation with nitric acid followed by impregnation with urea (10 %) and heat treatment at 700 °C according to the method developed previously for active carbons [6].

The synthesized N-CNTs contain a certain amount of amorphous carbon and catalyst components. Purification of the original samples was performed by treating them with HCl solutions and NH_4HF_2 followed by washing the reagents with distilled water.

In kinetic experiments, aqueous solutions of hydrogen peroxide with a concentration of 0.1–0.5 % were used to study the catalytic properties of N-CNTs synthesized from ethylenediamine and 0.2–1.5 % to determine the properties of N-CNTs synthesized from acetonitrile. The experiments were performed at pH 5.0, 6.0, 7.0, 8.0, which were stabilized with phosphate buffer and at room temperature. Stable suspensions of N-CNTs were used for the reaction. To do this, samples were dissolved in phosphate buffer (the volume of the solution

varied as dependent on the concentration of H_2O_2 in the reaction mixture). Hydrogen peroxide was then added to the suspension so that the total volume of the reaction mixture was 50 ml. In the case of N-CNTs, the process of H_2O_2 decomposition was investigated using the microvolumetric method [19]. The experiments were performed in a sealed thermostated cell with stirring connected to a microburette (measurement error 0.01 ml), which was used to measure the microvolumes of oxygen released during the reaction. In the study of catalase activity used a standard method for

determining the concentration of H_2O_2 – titrimetry [3, 19]. Evaluation of catalytic activity was performed by determining the kinetic characteristics (rate constants, Michaelis’ constants) of this reaction [3, 19]. To compare the values of the reaction rate constants for all objects, the optimal sample and the optimal range of H_2O_2 concentrations were chosen, at which the reaction rate linearly depends on the substrate concentration. To determine the reaction rate constant, the rate of decomposition of hydrogen peroxide at different pH was measured.

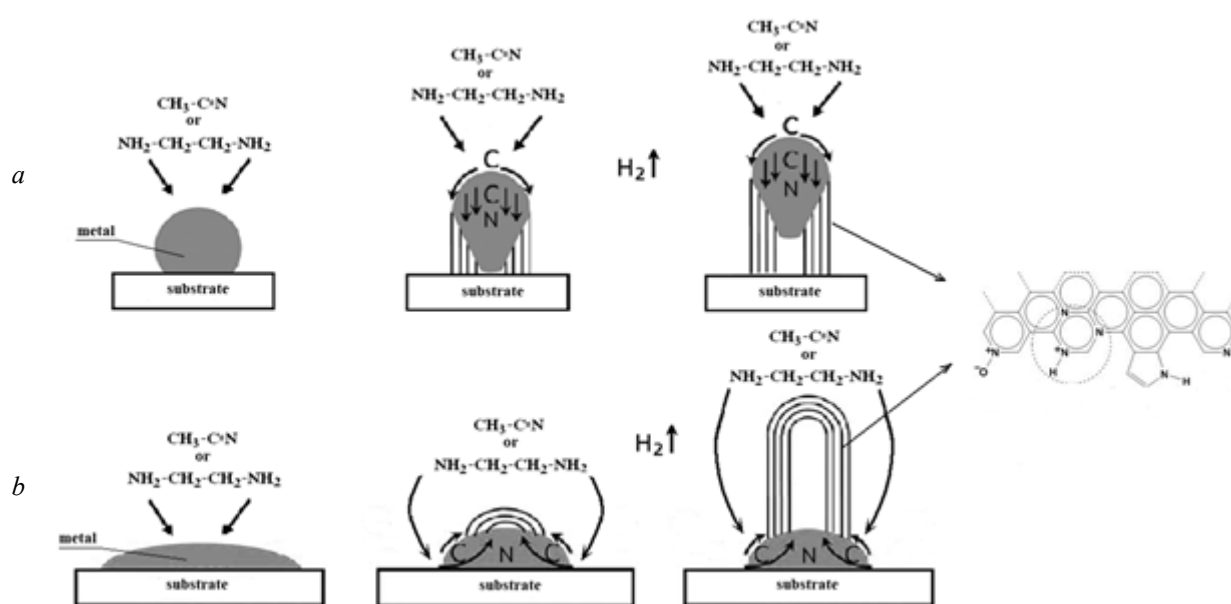


Fig. 2. Scheme of the growth of nitrogen-doped CNT: *a* – “top” model for the growth of CNT; *b* – “root” model for the growth of CNT

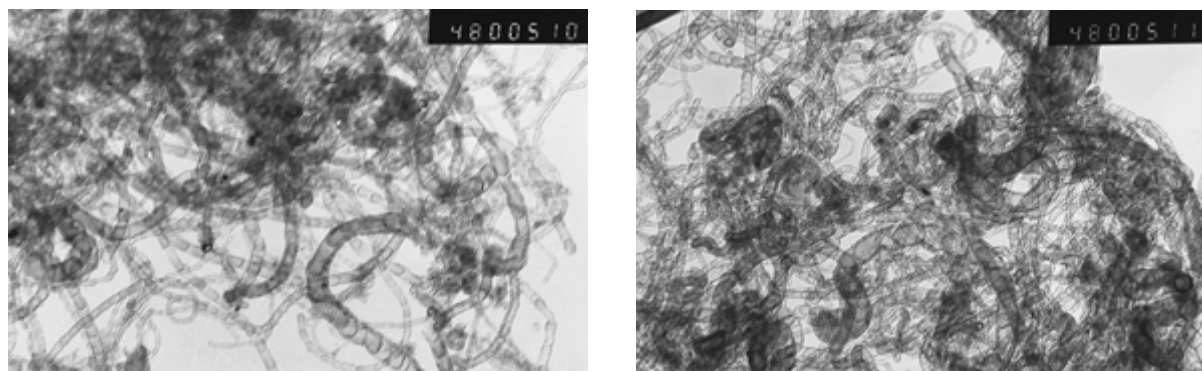


Fig. 3. TEM images of product obtained from 100 % acetonitrile

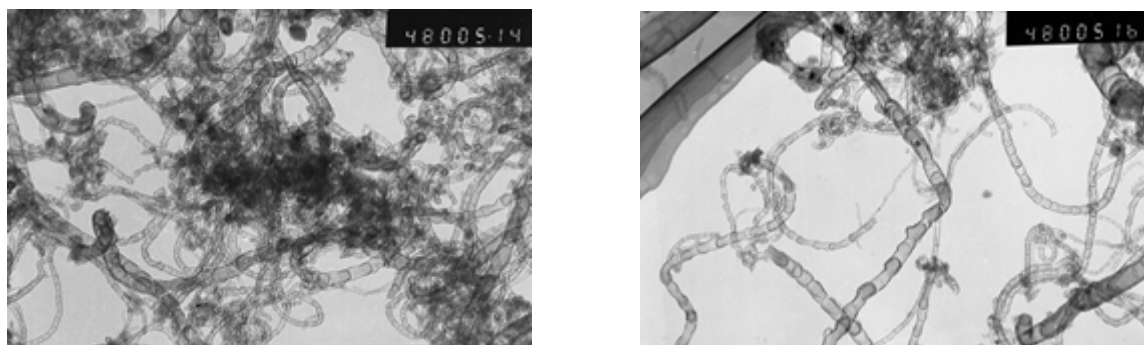


Fig. 4. TEM images of product obtained from 100 % ethylenediamine

Characterization of N-CNTs. The structural state of CNTs specimens was characterized by the Raman scattering method. Raman spectra of CNTs was recorded by a Horiba Jobin-Yvon T-64000 spectrometer in combination with the geometry of inverse scattering at room temperature when excited by an argon laser ($\lambda = 514.5$ nm, 1 mV). The measurements are depicted in Fig. 5. As a standard for calibrating the wavelength, Raman spectra band of silicon was used at 520 cm^{-1} . The experimental error of

determining the wavelength of the reflected radiation associated with the heterogeneity of the samples was 2 cm^{-1} .

The Raman spectra of N-CNTs differ significantly (Fig. 5) from the spectra of the initial carbon nanotubes. The intensity of the spectra drops sharply. The main parameters of the characteristic bands, which are manifested in the micro-Raman scattering of initial CNTs and obtained with the participation of acetonitrile and ethylenediamine, are presented in the Table 1.

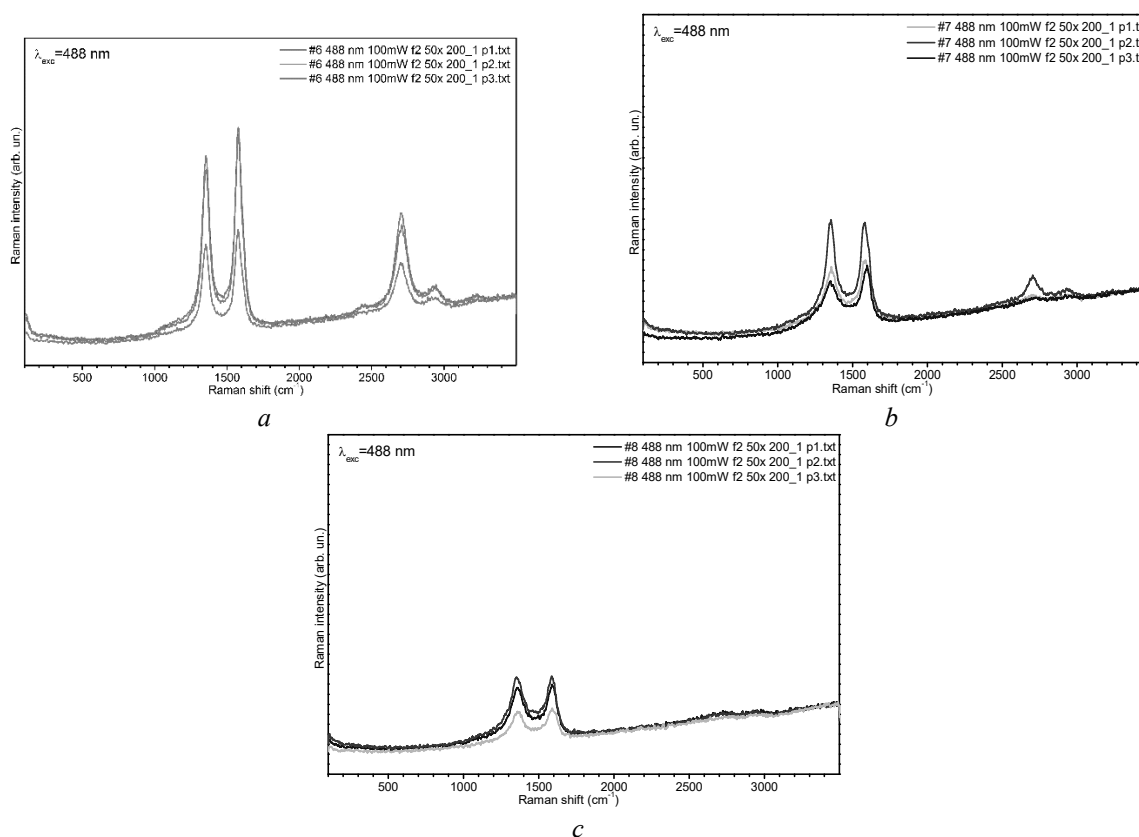


Fig. 5. The Raman spectra of CNTs: *a* – initial CNTs; *b* – CNTs obtained with using acetonitrile; *c* – CNTs obtained with using ethylenediamine

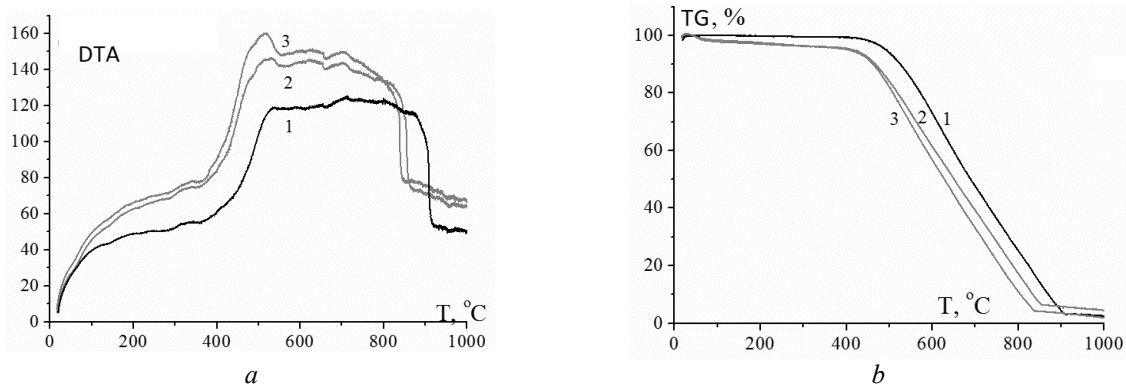
Table 1. The main parameters of the characteristic bands manifested in the micro-Raman scattering of initial CNTs and CNTs obtained with the participation of acetonitrile and ethylenediamine

Specimen Synthesis conditions	initial CNTs	N-CNTs (ethylenediamine)	N-CNTs (acetonitrile)
	Catalyst Al-Fe-Mo-O, synthesis at T , °C:		
	650	750	750
D , cm^{-1}	1348	1353	1353
G , cm^{-1}	1573	1580	1585
$2D$, cm^{-1}	2706	2705	–
D_{FWHM} , cm^{-1}	51	80	112
G_{FWHM} , cm^{-1}	53	75	108
I_D , a.u.	9.0	5.0	3.1
I_G , a.u.	10.4	4.7	3.0
I_D/I_G	0.86	1.06	1.03

As can be seen from the Raman spectra for CNTs (Table 1), the frequency D (1353 cm^{-1} for both samples) of the band is significantly higher than the original CNTs (1348 cm^{-1}). Similarly, the frequency G of the band for both samples increases compared to output CNTs, and higher for the sample with the calculated content of N-CNT, acetonitrile. This indicates a strong tension of the CNT lattice, which can be understood if nitrogen is actually embedded in the ‘body’ of the CNTs. The half-widths of the bands increase considerably, which indicates a

significant disorder in the structure of this product. It can be argued that the synthesis with the participation of nitrogen compounds improves the fragmentation of CNTs.

From the analysis of DTA diagrams (derivatograph Q-1500D, Hungary) (Fig. 6) one can draw a conclusion, that the intensive oxidation of nitrogen-containing structures begins at 100 °C earlier than for the original CNTs. However, the heat capacity of this process is significantly higher than for CNTs.


Fig. 6. CNT derivatograms: *a* – DTA; *b* – TG; *1* – initial CNT’s; nanotubes synthesized with the participation of: *2* - acetonitrile; *3* – ethylenediamine

To determine the chemical composition of the CNTs obtained by us, the method of X-ray photoelectron spectroscopy (XPS) was applied. The state of the surface of the washed from mineral impurities and dried CNTs were investigated on an XPS spectrometer “SERIES-800” Kratos Analytical using monochromatic MgK_α -radiation with energy of 1253.6 eV .

According to the obtained results (Table 2), treatment of oxidized CNTs samples with urea

leads to the appearance of 0.6 at. \% nitrogen in their structure. Despite the fact that the vast majority of nitrogen atoms are on the side surfaces of CNTs, as well as located along the surface.

When modifying CNTs by directly introducing ethylenediamine and acetonitrile in the liquid state into a stream of argon and hydrogen carrier gas, we observe an increase in the number of nitrogen atoms embedded in the structure of nanotubes. When nitrogen atoms are

included in a carbon nanotube (precursor-acetonitrile), we observe a 5-fold increase in the hetero atom and 7 times an increase in case of precursor - ethylenediamine.

From the N1s spectra (Fig. 7) of the obtained nitrogen-containing CNTs, one can see how the state of nitrogen atoms changes depending on the conditions of their synthesis (Table 3).

Table 2. Chemical composition of the surface of synthesized nanotubes (at. %)

Sample	C, at. %	O, at. %	N, at. %
CNTs	98.78	1.22	0.00
N-CNTs (urea)	98.27	1.11	0.62
N-CNTs (acetonitrile)	95.13	1.86	3.22
N-CNTs (ethylenediamine)	93.68	1.65	4.46

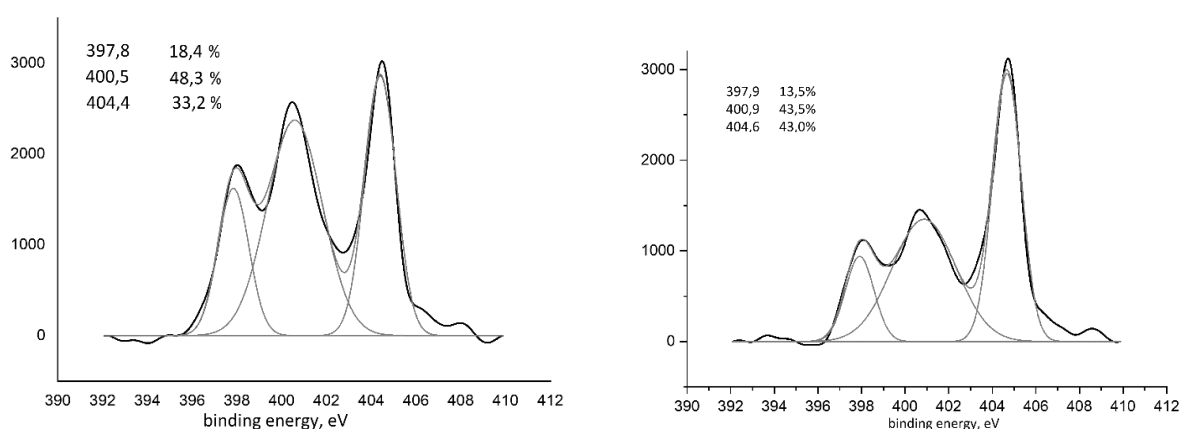


Fig. 7. XPS N1s spectra of nitrogen containing CNTs: *a* – synthesized with the participation of ethylenediamine; *b* – synthesized with the participation of acetonitrile

Table 3. The content and chemical state of nitrogen and oxygen atoms in CNT depending on the nitrogen-containing compound used for CNT synthesis

No	Sample	Pyridinic, at. %	Pyrrolic and Quaternary, at. %	N-oxide, at. %	N, at. %
1	N-CNTs (urea)	51.6	33.9	14.5	0.62
2	N-CNTs (acetonitrile)	13.5	43.5	43	3.22
3	N-CNTs (ethylenediamine)	18.4	48.3	33.2	4.46

From the above data, it can be seen that in the direct synthesis of nitrogen-containing CNTs, not only the total content of nitrogen atoms but also the proportion of pyrrolic and quaternary nitrogen increases significantly against the background of a significant decrease in the amount of the pyridinic form. This can be explained by the fact that, in direct synthesis, nitrogen is uniformly distributed over the entire volume of the carbon matrix of CNTs, and during nitriding of CNTs

with urea, predominantly in the surface layers and near defects. Since the pyridinic form is characteristic of the edge arrangement of the nitrogen atom in the graphene plane, it is obvious that for samples with a uniform distribution of nitrogen in the volume, the ratio between pyridinic and pyrrolic/quaternary will be shifted towards the latter.

Catalytic properties of N-CNTs. From the data obtained during the catalytic decomposition

of hydrogen peroxide on initial and nitrogen-modified CNTs, the reaction rate constants and affinity coefficients were calculated at different pH solutions. Based on these data, the corresponding dependences were built (Fig. 8).

The given dependences (Fig. 8) show that for all pH values nitrogen-containing CNTs show greater activity in catalysis of hydrogen peroxide decomposition than unmodified tubes. The

catalytic activity rapidly increases with an increase in the content of nitrogen heteroatoms, which fully corresponds to theoretical models of the effect of heteroatoms on the electron-donating properties of the carbon matrix. It should also be noted that nitrogen-containing CNTs reach their maximum catalytic activity at pH values close to 7, which is important for the use of such materials for catalysis in biological media.

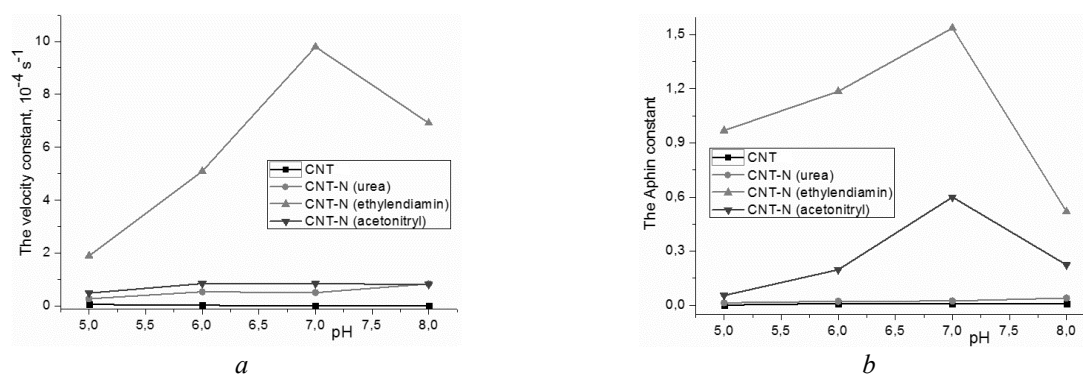


Fig. 8. The velocity constant (a) and the A_{aff} constant (b) vs. pH for different CNTs

CONCLUSION

From the data obtained, it can be concluded that the method of direct synthesis of nitrogen-containing CNTs makes it possible to obtain more catalytically active carbon nanotubes containing a

larger amount of nitrogen, predominantly of the pyrrole and quaternary type. It was found that, regardless of the synthesis method, the maximum catalytic activity in the decomposition of hydrogen peroxide is observed at pH 7.

Синтез і каталітичні властивості азотовмісних вуглецевих нанотрубок

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Азотовмісні вуглецеві нанотрубки (ВНТ) синтезували CVD-методом на оксидних каталізаторах Al-Fe-Mo-O, додаючи в джерело вуглецю (пропілен) ацетонітрил або етилендіамін, або повністю його заміщуючи, а також просочуючи сечовиною вихідні ВНТ з подальшою термообробкою. Структура азотовмісних ВНТ характеризувалась методом комбінаційного розсіяння світла (КРС), трансмісійної мікроскопії (ТЕМ), диференціального термічного й гравіметричного аналізу (ДТА, ДТГ) і рентгенівської фотоелектронної спектроскопії (РФЕС). Встановлено вплив методу синтезу на кількість та хімічний стан гетероатомів азоту в структурі вуглецевої матриці. За результатами ТЕМ, азотовмісні ВНТ мають характерну бамбукоподібну структуру, що є менш досконалою в порівнянні з структурою вихідних ВНТ: характерні смуги (G і D) КРС зміщені в область вищих частот, збільшується їхня напівширина та інтенсивність смуги D відносно G. Це також проявляється в меншій термічній стійкості азотовмісних ВНТ.

За даними РФЕС, при безпосередньому синтезі азотовмісних ВНТ збільшується загальний вміст атомів азоту й частка пірольного та четвертинного на тлі значного зменшення кількості піридинової форми. Це можна пояснити тим, що азот рівномірно розподіляється по всьому об'єму вуглецевої матриці ВНТ, а під час азотування ВНТ сечовиною азот включається переважно в поверхневі шари та на дефектах, оскільки піридинова форма характерна для крайового розташування атома азоту в площині графену. Розглядається каталітичний вплив багатопірольних азотовмісних ВНТ на кінетику розкладання перекису водню у водних розчинах при різних значеннях рН. Зроблено висновок, що метод прямого синтезу азотовмісних ВНТ дозволяє отримати більш каталітично активні вуглецеві нанотрубки, що містять більшу кількість азоту, переважно пірольного та четвертинного типу. Також встановлено, що незалежно від методу синтезу максимальна каталітична активність при розкладанні перекису водню спостерігається при рН 7.

Ключові слова: азотовмісні вуглецеві нанотрубки, каталіз, перекис водню

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