ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

N E W S

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

2 (446)

MARCH – APRIL 2021

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген **№ KZ66VPY00025419** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: ***химия және жаңа материалдар технологиясы саласындағы басым ғылыми зерттеулерді жариялау.***

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-18, http://chemistry-technology.kz/index.php/en/arhiv

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Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия химии и технологий».

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан **№ KZ66VPY00025419**, выданное 29.07.2020 г.

Тематическая направленность: ***публикация приоритетных научных исследований в области химии и технологий новых материалов.***

Периодичность: 6 раз в год.
Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75.

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ66VPY00025419**, issued 29.07.2020.

Thematic scope: ***publication of priority research in the field of chemistry and technology of new materials***

Periodicity: 6 times a year.
Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: ST "Aruna", 75, Muratbayev str., Almaty.

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286
Volume 2, Number 446 (2021), 72 – 80 **https://doi.org/10.32014/2021.2518-1491.29**

UDC 678.03:546.26; 677.4
IRSTI 61.67.33

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PRODUCTION OF CARBON NANOFIBERS BASED ON COAL TAR AND POLYACRYONITRILE BY ELECTROSPINNING METHOD

Abstract. The article presents experiments on obtaining composite fibers based on Shubarkol coal tar (CT) and polycarlonitrile (PAN) by electrospinning in a laboratory setup. As a result of energy dispersive X-ray spectroscopy and SEM microscopy, the elemental composition (C-85.83%) and the diameter of the carbon fiber were determined, which ranged from 89.0 nm to 449.8 nm. The resulting CNF was subjected to oxidation in air at 300 °C, the holding time was 1 hour, after which the carbonization process was carried out at 800 °C, followed by cooling to room temperature. Raman spectra were recorded to study the degree of graphitization. The results of Raman scattering of light (RS) showed the degree of graphitization - 15.98%. Ratio I (D) / I (G) = 0.99, I (G) / I (D) = 1. The broad bands D (disordered part) and G (ordered graphite structure) suggest that CNFs contain partially graphitized carbon along with amorphous carbon. The ID / IG ratio represents the conversion of disordered carbon to graphite carbon during carbonization. The resistance of this material is 70-200 ohms. The results obtained confirm the semiconductor nature of the conductivity. On the basis of SEM drawings of CNFs from CT and PAN, it was found that the structure of CNFs after oxidation and carbonization retains the original fibrous structure. It was also found that the diameter of nanofibers decreases from 320.5 - 625.7 nm to 89-449.8 nm. Thus, the proposed method of obtaining CNF is built on the basis of the electrospinning method, which is the most promising method of industrial production.

Key words: carbon nanofiber, coal tar, polyacrylonitrile, electrospinning, oxidation, carbonization.

The development of new technologies and ensuring a sustainable level of consumption in conditions of depletion of raw energy resources requires the development of new systems and devices for autonomous power supply, widely used as auxiliary and backup elements in the energy sector, in power systems for transport, communications, in portable electronic devices, household and special technique. Most of these systems and devices belong to electrochemical power engineering, an actively developing area of modern science, closely related to chemical technologies [1].

Supercapacitors (SC) and capacitive deionization systems that can reversibly accumulate charge on the surface of the electrode material are promising devices for accumulating and storing electrical energy, combining both high energy intensity and relatively high output power [2].

Rechargeable lithium-ion batteries (LIB) play an important role in portable electronic devices due to their long lifespan and high energy density [3]. However, the lithium content in the earth's crust is only 20 g/t [4]. This, coupled with the uneven distribution of lithium minerals, has led to growing concerns about the scarcity of lithium resources [4]. On the other hand, sodium is the most abundant alkali metal in the oceans and is easily extracted from sea salt. The Na^+/Na redox potential is 2.71 V versus a standard hydrogen electrode versus 3.04 V for Li^+/Li. Due to the abundance of sodium resources and its large negative redox potential, sodium ion batteries (NIBs) have attracted more and more attention in the past few years [5-8].

However, the difference in size of the two types (68 hours for Li^+ and 95 hours for Na^+) means that the anode materials LIB and NIB cannot be interchanged [9]. In addition, in contrast to LIB, Na^+ ions

practically cannot intercalate into graphite [9, 10]. For LIB, the graphite anode after intercalation has the chemical formula LiC_6, while in the analogue of NIB the anode formula is NaC_{70} [11]. Thus, many examples have been applied for making appropriate anodes in other fields, such as disordered graphite carbon, also known as hard carbon [12]. Many of the proposed solutions used inexpensive, non-toxic and readily available solid solid materials, such as hierarchically porous carbon [12], carbon microspheres [13], carbon black [14], carbon nanostructures [15,16], graphene, nanocomposites [17] and carbon doped with nitrogen [18, 19]. After these effects, there are many unexplored solid carbon.

Nanotechnology is an increasingly viable method for changing the structure and properties of electrode materials [20-24]. In particular, one-dimensional carbon nanofibers have proven to be promising for improving the capacitance and cyclic performance of NIBs due to their good conductivity, short ion diffusion distances, and excellent stress resistance [15, 16]. The production of flexible, stand-alone carbon nanofiber electrodes, in which all materials participate in charge accumulation, is being investigated with the aim of further increasing the NIB power density [23]. This greatly simplifies the preparation process by eliminating inert current collectors and binders, which improves the electrochemical characteristics. There have been extensive studies of LIB nanomaterial electrodes [25-30], but few studies of NIB [31].

CNFs have attracted much attention of scientists for their potential thermal, electrical, shielding, and mechanical properties [32]. Due to their exceptional properties and low cost, they are now increasingly used in various materials such as composites. CNF-based composites can be used as promising materials in many fields, such as electrical devices, electrode materials for batteries and supercapacitors, and also as sensors.

The problem of utilization of coal-containing waste, as coal tar, is of particular relevance in large coal mining centers. Therefore, at present there is an urgent need to develop effective methods for the disposal of this waste as a secondary raw material resource.

Coal tar is one of the products of coal coking; viscous black liquid with a characteristic phenolic odor, density 1120-1250 kg / m^3, coking yield ~ 3% of the coal mass. Coal tar is a complex mixture of aromatic, heterocyclic compounds and their derivatives, boiling over a wide range of temperatures. More than 400 individual compounds have been isolated from coal tar, some of which are produced on an industrial scale. Individual substances are extracted from coal tar fractions either by crystallization or by treatment with reagents (for example, with an alkali solution in the extraction of phenols). The residues after extraction are industrial oils used as absorbents of benzene products from coke oven gas, for wood preservation, production of soot, and other purposes [33].

We used coal tar formed during pyrolysis of coal from the Shubarkol deposit, which has the following characteristics: density at 20 ° C - 1070 kg/m^3, viscosity at 80 ° C - 2.9-3.3 conventional degrees, coking capacity - 2.0-3.5%, flash point - 110-120 ° C, softening temperature - 60-70 ° C, volatile matter yield - 83.0%. It is not electrically conductive and insoluble in water, dissolves only in organic solvents (pyridine, benzene, etc.), and is resistant to acids [34].

The technology for producing carbon fiber based on coal tar includes several stages: substrate preparation, fiber synthesis by electrospinning, stabilization in an oxidizing atmosphere, carbonization in an inert atmosphere, graphitization at elevated temperatures.

Electrospinning is a process that leads to the formation of nanofibers as a result of the action of electrostatic forces on an electrically charged jet of a polymer solution or melt [35].

The essence of the electrospinning method is that an electric voltage from units to one hundred kilovolts is applied to a solution (melt), which is fed through a capillary with a dispenser [36]. High voltage induces in the solution the electric charges of the same name, which, as a result of the Coulomb electrostatic interaction, lead to the pulling of the polymer solution into a thin jet [37]. In the process of electrostatic stretching of a polymer jet, it can undergo a series of successive splits into thinner jets at a certain ratio of the values of viscosity, surface tension, and electric charge density in the fiber [38]. The resulting jets solidify due to solvent evaporation or as a result of cooling, turning into fibers and, under the action of electrostatic forces, drift to a grounded substrate, which has the opposite electric potential [39, 40].

The good thing about the electrospinning method is that, unlike the usual mechanical pulling of fibers from a solution, it does not impose high requirements on the chemistry of the process, does not require high temperatures for fiber solidification, which means that it allows you to create fibers from long and complex molecules. As a result of the struggle between capillary and electrostatic forces. Also, the

processes inside the solution, the charged drop itself lengthens, becomes thinner and dries up in flight. A typical electrospinning setup, as shown in figure 1, consists mainly of three components: a capillary tube with a small bore pipette or needle, a high voltage source, and a metal screen assembly.

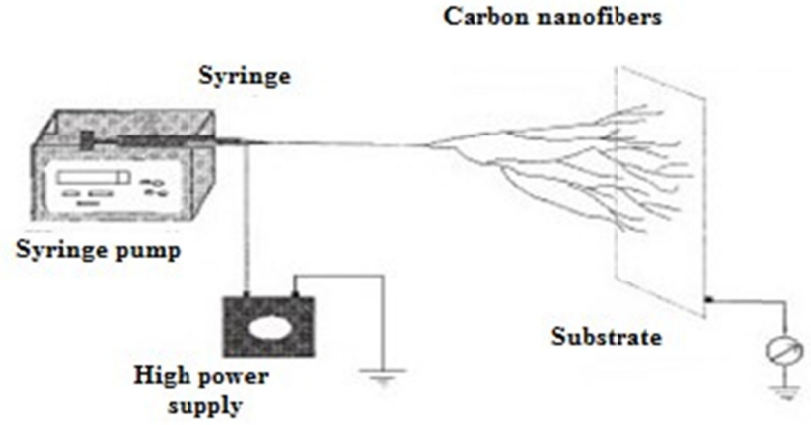


Figure 1 - Schematic diagram of an electrospinning installation with a stationary substrate

Based on the above, the goal of the forthcoming work was formulated, which is to obtain carbon fibers based on coal tar and PAN by the electrospinning method and to study their physical and chemical properties.

Research methodology. Samples of composite CNF were obtained at the Institute of Chemistry and Technology of Coal LLP (Nur-Sultan) by electrospinning in laboratory conditions. Coal tar from coal from the Shubarkol deposit and polyacrylonitrile (PAN) were used as feedstock.

The following instruments were used in the study: an ultrasonic bath, a laboratory electrospinning apparatus, an SEM (Quanta 3D 200i) with an energy dispersive analysis attachment from EDAX, and Raman spectroscopy (HORIBA Jobin Yvon).

The method of obtaining carbon nanocomposite fibers from coal tar by the electrospinning method includes the following stages: preparation of raw materials, formation, stabilization (oxidation - to remove low molecular weight products of destruction and the formation of crosslinked and cyclic structures) and carbonization (to remove hydrogen and heteroatoms in the form of volatile compounds, where final formation of carbon fibers).

To obtain carbon nanofibers, coal tar from the Shubarkol deposit and polyacrylonitrile (PAN) in a 1:1 ratio are dissolved in N, N-dimethylformamide in an oven at a temperature of 50-80 °C. The prepared solutions are placed in an electrospinning installation with a syringe, the set voltage is 20-25 kV, the distance between the syringe receiver is 30-35 cm (figure 2).

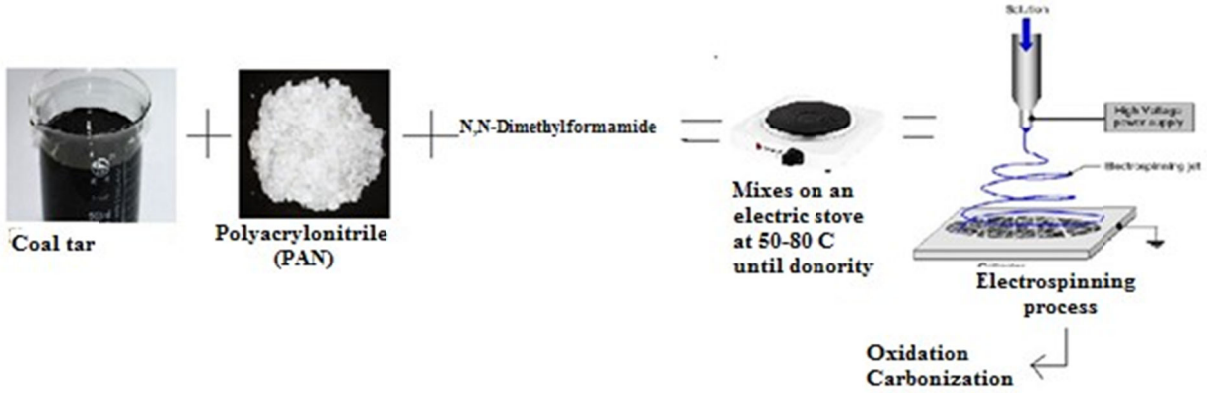
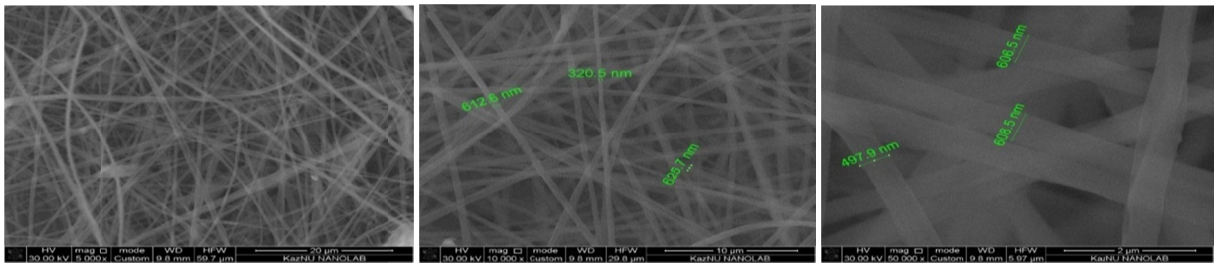


Figure 2 - Technological scheme for the synthesis of carbon nanofiber based on coal tar and PAN

CNF obtained after spinning are oxidized at a temperature of 300 °C in an air stream, the holding time is 1 h, after oxidation, the carbonization process is carried out in an inert argon atmosphere at a temperature of 800 °C, the heating rate is 5 °C/min, the holding time is 60 minutes [41- 42].

Results and discussion.

The results of the scanning electron microscope are shown in figure 3.



a) b) c)

Figure 3 - Electron microscopic images of CNF samples from coal tar and PAN:
a) x5000, b) x10000, c) x50000 on a scanning electron microscope

Figure 3 clearly shows CNF particles with diameters from 320.5 nm to 625.7 nm. Structural elements of nanofibers take the form of threadlike formations. The cylindrical surface of the fibers is formed by hexagons. The elemental composition of CNFs on the surface of an aluminum foil is shown in figure 4.

Element	*Wt%*	*At%*
C	66.76	81.83
O	0.38	0.35
Al	32.11	17.52
Si	0.42	0.22
Fe	0.33	0.09

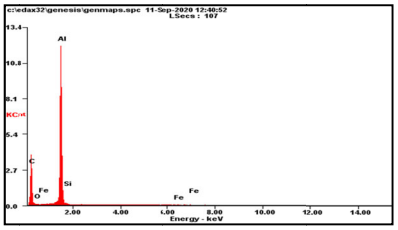
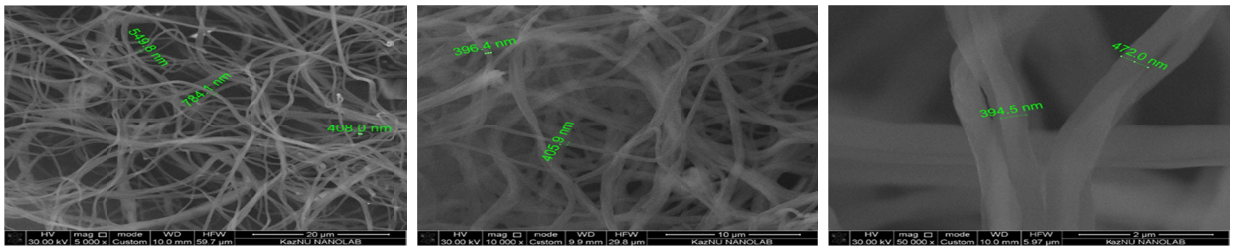


Figure 4 - Elemental analysis of the obtained CNF based on coal tar and PAN

Further, studies are carried out on the oxidation and carbonization of the obtained CNF, since the spun fiber, as a rule, is characterized by low strength and increased fragility. For this, CNFs were oxidized at a temperature of 300 ° C in an air flow in a laboratory quartz reactor at a heating rate of 5 ° C / min, the holding time was 1 hour. During it, low molecular weight degradation products are removed and crosslinked and cyclic structures are formed. SEM images of the oxidized form of CNF are shown in figure 5.



a) b) c)

Figure 5 - Electron microscopic images of a sample of oxidized CNF
from coal tar and PAN: a) x5000, b) x10000, c) x50000

Oxidized at 300 ^{0}C CNF from coal tar and PAN has a diameter from 394.5 nm to 784.5 nm. Carbon nanofibers are predominantly circular in cross-section and fibrillar structure. Each monofilament consists of fibrils parallel to each other. The elemental composition of carbon increased after the oxidation process by 90.49% in comparison with the initial CNF.

Element	Wt%	At%
C	90.49	92.76
O	9.30	7.16
Si	0.10	0.04
S	0.11	0.04

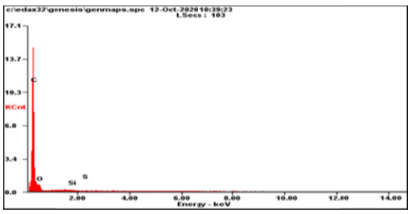
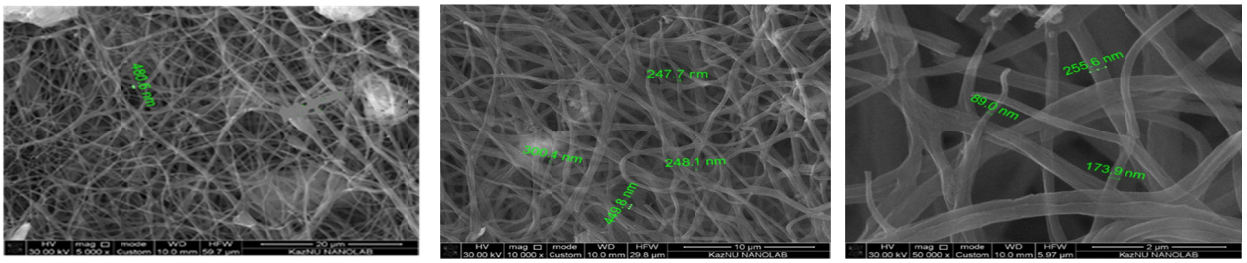


Figure 6 - Elemental analysis of oxidized CNF from coal tar and PAN

In the subsequent stages of high-temperature treatment - carbonization at 800 °C, accompanied by the removal of hydrogen and heteroatoms in the form of volatile compounds, the final formation of carbon nanofibers occurs. The oxidized fibers were carbonized at 800 ° C, the heating rate was 5 ° C/min in an argon atmosphere, the holding time was 1 h (figure 7).



a) b) c)

Figure 7 - Electron microscopic images of a sample of carbonized CNF from coal tar and PAN:
a) x5000, b) x10000, c) x50000 on a scanning electron microscope

CNF carbonized at 800 °C from coal tar and PAN has a diameter from 89.0 nm to 449.8 nm. Figure 7 shows the surface of CNF, which represents a fibrillar structure. Small bumps are also visible on the surface. Sizing “strands” are also observed between the fibers, linking the individual filaments to each other. The carbon content is 85.83% (figure 8).

Element	Wt%	At%
C	85.83	89.32
O	13.09	10.23
Na	0.17	0.09
Mg	0.11	0.06
Al	0.11	0.05
Si	0.14	0.06
S	0.24	0.09
Cl	0.08	0.03
Ca	0.24	0.08

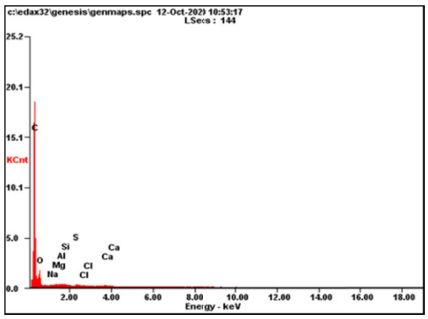


Figure 8 - Elemental analysis of carbonized CNF from coal tar and PAN

The results of Raman scattering of light (RS) showed the degree of graphitization - 15.98%. The ratio I (D)/I (G) = 0.99, I (G)/I (D) = 1 (figure 9). Raman spectra were recorded to study the degree of graphitization. The broad bands D (disordered part) and G (ordered graphite structure) suggest that CNFs contain partially graphitized carbon along with amorphous carbon. Graphitized carbon usually consists of assemblies of graphite layers that are expected to act to store ions. The ratio of the relative intensity (ID/IG) of the D and G bands indicates the degree of disorder in the carbon structure. As shown in figure 9, the ID/IG ratio represents the conversion of disordered carbon to graphite carbon during carbonization.

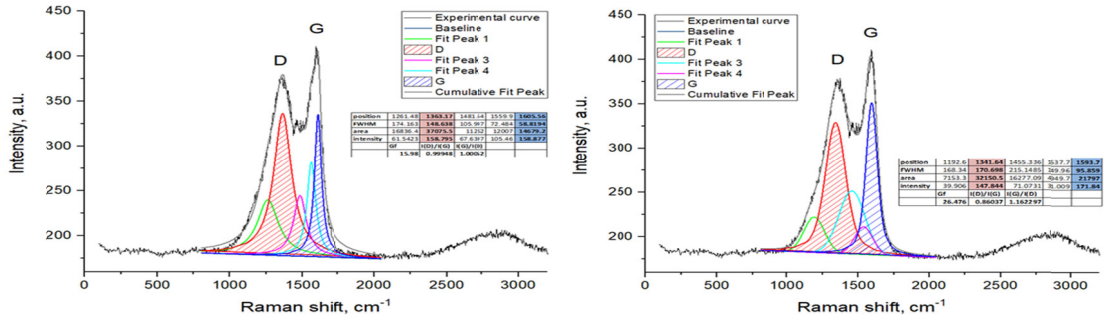


Figure 9 - Raman images of a carbonized CNF sample from CT + PAN: (a) according to Lorentz - Gf = 15.98%, I (D) / I (G) = 0.99, I (G) / I (D) = 1 (Lorentz) ; (b) Voigt - Gf = 26.47%, I (D) / I (G) = 0.86, I (G) / I (D) = 1.16 (Voigt)

The resistance of this material is 70-200 ohms. The results obtained confirm the semiconductor nature of the conductivity.

On the basis of SEM drawings of CNFs from CT and PAN, it was found that the structure of CNFs after oxidation and carbonization retains the original fibrous structure. It was also found that the diameter of nanofibers decreases from 320.5 - 625.7 nm to 89-449.8 nm, which may be associated with the release of volatile and heterogeneous components of the original product and the formation of a more structural thin porous filament.

Thus, the proposed method for producing CNFs is based on the electrospinning method, which is the most promising method of industrial production. The proposed method is unique in that the raw material (CT), which we use to obtain carbon nanofibers, is a renewable resource, in comparison with the technology for producing fibers from many other precursors (nylon, polyester, acrylic, polypropylene, etc.). The prospect of these studies lies in the possibility of large-scale production of carbon nanofibers from coal tar, which will lead to the appearance of domestically produced materials and composites based on them on the Kazakhstan market.

If Kazakhstan producers provide a high quality product that meets all consumer requirements, the need for imports of CNF will decrease. Unique properties allow the use of carbon nanofiber in various areas of human life. However, at the moment, industrial technologies for the production of functional carbon nanofiber from coal tar are only under development.

Acknowledgement. This work was carried out as part of the scientific and technical program No. IRN BR05236359 “Scientific and technological support for coal processing and production of high-value coal products” and project No. IRN AP05130707 on the theme “Development of technology and creation of production of carbon nanocomposite materials based on domestic mineral raw materials for gas phase urification and wastewater”, funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

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ТАС КӨМІР ШАЙЫРЫ МЕН МЕН ПОЛИКАРИЛОНИТРИЛ НЕГІЗІНДЕ ЭЛЕКТРОСПИННИНГ ӘДІСІМЕН КӨМІРТЕКТІ НАНОТАЛШЫҚТАРДЫ ӨНДІРУ

Аннотация. Мақалада зертханалық қондырғыда электроспиннинг әдісімен "Шұбаркөл" таскөмір шайыры (ТКШ) және поликарилонитрил (ПАН) негізінде композитті наноталшықтарды алу бойынша тәжірибелер жүргізілді. Рентгендік спектроскопия және СЭМ-микроскопия нәтижесінде элемент құрамы (С-85,83 %) және көміртек наноталшығының диаметрі анықталды, ол 89,0 нм-ден 449,8 нм-ге дейін құрады. Алынған КНТ ауада 300°С температурада тотығуға ұшырады, ұстау уақыты 1 сағатты құрады, көміртектену процесі 800°С температурада жүргізілді, содан кейін бөлме температурасына дейін салқындатылды. Графиттеу дәрежесін зерттеу үшін раман спектрлері жазылды. Жарықтың комбинациялық шашырауының

(ЖКШ) графиттеу дәрежесін көрсетті - 15,98%. I (D) / I (G) = 0.99, I (G) / I (D) = 1. D (тәртіпсіз бөлік) және G (графиттің құрылымы бойынша) кең жолақтар CNF құрамында аморфты көміртекпен бірге ішінара графиттелген көміртек бар деп болжайды. ID / IG коэффициенті карбонизация кезінде ретсіз көміртектің графитті көміртекке айналуын білдіреді. Бұл материалдың кедергісі 70-200 Ом құрайды. Алынған нәтижелер материалдың жартылай өткізгіштігін білдіреді. ТКШ және ПАН-ден алынған КНТ тотығу мен карбонизациядан кейін бастапқы талшықтың құрылымын сақтайтындығы анықталды. Наноталшықтардың диаметрі 320,5 - 625,7 нм-ден 89-449,8 нм-ге дейін азаятындығы анықталды. Осылайша, КНТ өндірудің ұсынылған электроспиннинг әдісі өнеркәсіптік өндірістің ең перспективалы әдісі болып табылады.

Түйін сөздер: көміртекті наноталшық, тас көмір шайыры, полиакрилонитрил, электроспиннинг, тотығу, карбонизация.

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ПОЛУЧЕНИЕ УГЛЕРОДНЫХ ВОЛОКОН НА ОСНОВЕ КАМЕННОУГОЛЬНОЙ СМОЛЫ И ПОЛИАКРИОНИТРИЛА МЕТОДОМ ЭЛЕКТРОСПИННИНГА

Аннотация. В статье приведены результаты экспериментов по получению композитных волокон на основе каменноугольной смолы «Шубарколь» и поликарилонитрила (ПАН) методом электроспиннинга в лабораторной установке. В результате энергодисперсионной рентгеновской спектроскопии и СЭМ-микроскопии был определен элементный состав (С-85,83 %) и диаметр углеродного волокна, который составил от 89,0 нм до 449,8 нм. Полученный УНВ подвергался окислению на воздухе при 300 °С, время выдержки 1 час, после проводен процесс карбонизации при 800 °С, с последующим охлаждением до комнатной температуры. Спектры комбинационного рассеяния были записаны для изучения степени графитизации. Результаты комбинационного рассеяния света (КРС) показали степень графитизации – 15,98 %. Соотношение I(D)/I(G)=0,99, I(G)/I(D)=1. Широкие полосы D (неупорядоченная часть) и G (упорядоченная графитовая структура) предполагают, что УНВ содержат частично графитизированный углерод наряду с аморфным углеродом. Соотношение ID / IG представляет преобразование неупорядоченного углерода в графитовый углерод в процессе карбонизации.Сопротивление данного материала составляет 70-200 Ом. Полученные результаты подтверждают полупроводниковый характер проводимости. На основание СЭМ рисунков УНВ из КУС и ПАН установлено, что структура УНВ после окисления и карбонизации сохраняет исходную волокнистую структуру. Также было обнаружено, что диаметр нановолокон уменьшается от 320,5 - 625,7 нм до 89-449,8 нм. Таким образом, предлагаемый способ получения УНВ построен на основе метода электроспиннинга, который является наиболее перспективным способом промышленного производства.

Ключевые слова: углеродное нановолокно, каменноугольная смола, полиакрилонитрил, электроспиннинг, окисление, карбонизация.

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ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Д. С. Аленов, Р.Ж. Мрзабаева*
Верстка на компьютере *Д. А. Абдрахимовой*

Подписано в печать 12.04. 2021.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
10,2 п.л. Тираж 300. Заказ 2.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19