Catalytic Synthesis of Graphite Oxide and Graphite Nanostructures in Transient Glow-to-Arc Plasma Discharge

Carbon and carbon-based materials like graphene and graphite oxide exhibit a constantly expanding field of applications in science, medicine, and industry. However, their implementation is still hindered by the absence of a reliable, flexible, and highly productive method of synthesis. Most of the existing methods rely on the use of chemical reagents potentially dangerous for the environment. In this paper, a physical method based on the use of a transient glow-to-arc discharge is developed, and the carbon nanostructures are obtained during a single-step production in a plasma reactor. Argon and oxygen are used to grow either carbon or carbon oxide nanostructures on the surfaces of expanded graphite samples. To enhance the growth of the carbon nanostructures, an anode made of copper is employed in the setup, to serve as a source of the copper catalyst. As a result, complex three-dimensional carbon nanostructures with a density of about 0.01 μm^{-2} were detected using scanning electron microscopy (SEM) on the entire surface of the sample after the oxygen plasma treatment. An enlarged view of nanostructures shows that they are a composition of 2D and 1D nanostructures connected by jumpers, as well as the presence of tree-like and petal nanostructures with dimensions of approximately 3 μm in length and 30 nm in diameter. The replacement of oxygen with argon led to a significant change in the appearance of nanostructures. Layered 2D graphene-like and tree-like carbon nanostructures capped with copper particles of diameters up to 10 μm were found. The obtained nanostructures suggest that expanded graphite is an excellent source for the production of two-dimensional nanostructures, like graphene and graphene oxide, which can be used as components for field-effect transistors, nanofluidic applications, supercapacitors, and electromagnetic absorbers.

Keywords: plasma; glow discharge; vacuum arc; nanotechnology; carbon nanostructures.

Introduction

Graphene and graphene oxide are 2D nanomaterials that are in demand for various applications for their outstanding properties. Graphene is characterized by a planar hexagonal lattice structure with the electrical conductivity over $10^6$ S/cm, Young’s modulus up to 1100 GPa, transmittance for visible light of about 97.9%, and the specific surface area as high as 2630 m$^2$/g [1]. Unlike graphene, graphene oxide contains many functional groups of oxygen, and that is why the properties of graphene oxide depend on its structure. The biomedical applications of graphene and its derivatives include its use in gene and drug delivery [2], and according to the research conducted by Liu et al. [3], graphene-based nanomaterials have an excellent effect on cement-based materials, which can be applied for preparation of high-performance building materials. Graphene and other carbon nanostructures have gained significant attention of a scientific community as electromagnetic wave absorbing [4] and shielding [5] materials in the high-frequency range. Superlubricity, when the dynamic friction coefficient is lower than 0.01, is also a feature of such carbon-based materials as diamond-like, onion-like, fullerene-like carbons, ultrananocrystalline diamonds, carbon nanotubes, and carbon nanostructures associated with liquid [6]. Typical values of the field enhancement factor in the range of $3 \times 10^4$ to $5 \times 10^4$ can be obtained in the individual carbon nanotubes that possess very sharp tips, while hybrid graphene nanostructures have the enhancement factor from 4000 to 6500, which makes the materials a perfect candidate for field-emitting applications [7]. Porous carbon nanostructures decorated with transition metal species are considered as substitutes of noble metals in enhancing catalytic performance in oxygen reduction reactions [8]. Functionalized fluorescent carbon nanostructures for targeted imaging of cancer cells were also reported [9]. Graphene oxide membranes exhibit a great potential for desalination of water purification; moreover, they show no damage in water, acid, and basic solutions even after months [10]. A review of catalytic properties of these materials with respect to wastewater purification was conducted by Thakur and Kandasubramanian [11]. A review carried out by Lim et al. [12] reported about the successful application of graphene and graphene oxide nanomaterials for removal of heavy metals from wastewater. A comprehensive review of electrochemical energy storage devices using graphene oxide was reported by Lian et al. [13]. At the same time, the applications of graphene oxide integrated photonic devices was proposed by Wu et al. [14]. Gra-
phene and graphene oxide are also considered as perspective materials for development of corrosion protective films and coatings [15]. At that, the researchers reached a consensus that a perfect graphene film protects the metal matrix well, but its protective performance is significantly reduced once the graphene film is damaged. Thus, a problem of obtaining very large substrates covered by the graphene films emerges. As for the ways of use the graphene-based materials, usually they are arranged in three different ways [16]: layering graphene components within composites with respect to improve the performance of applications such as electrodes, use as a filler material to aid in electrical and thermal conduction, e.g., and functionalising graphene derivatives to create hybrid nanostructures. Since the production of cheap high-quality graphene at an industrial scale remains a tremendous challenge, graphene oxide, which can be produced in desirable quantities and at low cost, is considered as a suitable substitute for the pristine graphene. Unfortunately, most of methods of the synthesis of graphene oxide use strong oxidants and results in generation of a large number of defects in its crystalline structure. To regain the graphene-like properties, graphene oxide is treated with the different techniques that transform it to the reduced graphene oxide that is considered as a very good compromise between graphene and graphene oxide with respect to the graphene distinguishing properties and simplicity of production of graphene oxide [17]. In addition, recently proposed methods for preparation of graphene oxide make it suitable for energy storage and utilization of nuclear wastes [18]. Various methods are developed to grow graphene oxide and reduced graphene oxide. Al-Gaashani et al. reported facile and safe methods to synthesize the species without the production of toxic and explosive gases, when the synthesized materials were strongly dependent on the mixture of acids [19]. Among the proposed approached, on-surface synthesis of carbon nanostructures appears to be the most developed [20], which can be explained by the fact that usually a substrate is an efficient third body in various chemical reactions.

**Formulation of the problem**

Thus, a problem of fast, flexible, and large-yield production of carbon and graphene materials still exists in spite of the fact that large number of techniques is already proposed. Most of them are based on chemistry that can be a source of hazardous agent causing environmental problems. That is why a plasma-enhanced physical method [21, 22] is developed and described in the present paper. Based on the literature analysis, on-surface synthesis of graphene materials is conducted on a substrate at presence of catalyst metal.

**Experimental part**

To perform the experiments on the growth of the carbon nanostructures, a plasma reactor utilizing the glow discharge plasma with the ability to survive its transition to the arc mode was used. The diameters of the anode and cathode were 15 mm and 35 mm, respectively, and the discharge gap was set to 20 mm. At that, the cathode was made of graphite, while the anode was made of copper to ensure the growth of the carbon nanostructure by use of copper catalyst. A vacuum chamber with a diameter of 300 mm and height of 350 mm was used to host the electrodes. To obtain the nanostructures, the samples made of the expanded graphite sheet with a diameter of 35 mm and a thickness of 1 mm were put on the cathode. A schematic of the experimental setup is shown in Fig. 1.

![Fig. 1. A schematic of the experimental setup](image1)

To grow the graphite oxide nanostructures, the vacuum chamber was filled with oxygen at the pressure of 230 Pa, and the glow plasma discharge was maintained for 20 minutes at the voltage drop of 780 V between the electrodes and the current of 0.12 A. For the synthesis of graphite nanostructures, argon was used at the pressure of 180 Pa as the background gas to ignite the plasma glow. In this case, the samples were treated for 30 minutes in argon plasma at the voltage drop of 750 V and the current of 0.13 A. A photograph of the glow discharge is shown in Fig. 2.

![Fig. 2. A photograph of the plasma discharge](image2)
In both cases, the samples were heated to dark red, and their temperatures was estimated as 650 °C. A large number of arcs with a period of 3 to 5 s was generated on the surface of the samples during the treatment.

After the plasma oxidation, the samples were passed to the scanning electron microscopy (SEM) to study the effect of the plasma treatment to the surface of the sample.

**Results and discussion**

Fig. 3 shows the scanning electron microscopy (SEM) images of a sample of expanded graphite treated in oxygen plasma for 20 minutes under the oxygen pressure of 230 Pa. Complex three-dimensional carbon nanostructures with a density of about 0.01 μm^{-2} were detected on the entire surface of the sample (Fig. 3, a).

Fig. 3. SEM image of a sample of expanded graphite treated in oxygen plasma for 20 minutes (230 Pa, 780 V and 0.12 A): a – three-dimensional carbon nanostructures with a density of about 10^{-2} μm^{-2}; b – enlarged view of 3D nanostructures, which are a composition of 2D and 1D nanostructures; c – the complex nature of the interaction of individual nanostructures connected by jumpers; d – tree-like nanostructures; e – petals with branches; f – an enlarged view of the nanostructure measuring approximately 3 μm in length and 30 nm in diameter.
An enlarged view of these 3D nanostructures shows that they are a composition of 2D and 1D nanostructures (Fig. 3, b). The complex nature of the interaction of individual nanostructures connected by jumpers (Fig. 3, c), as well as the presence of tree-like (Fig. 3, d) and petal nanostructures with processes (Fig. 3, e) was revealed. The enlarged view allows distinguishing the nanostructures with dimensions of approximately 3 μm in length and 30 nm in diameter (Fig. 3, f). The next set of samples made of expanded graphite was treated in argon plasma at a pressure of 180 Pa at a discharge voltage of 750 V and a current of 0.13 A. The replacement of the gas led to a significant change in the appearance of the nanostructures. General view of the nanostructures with a density of 0.04 μm⁻² on the surface of the sample is shown in Fig. 4, a.

Fig. 4. SEM image of a sample of expanded graphite treated for 30 minutes in argon plasma (180 Pa, 750 V and 0.13 A); a – general view of nanostructures with a density of 0.04 μm⁻² on the surface of the sample; b – enlarged view of the nanostructures, which shows their inhomogeneous distribution on the surface; c – layered carbon nanostructures; d – copper particle with a diameter of 10 μm with a developed system of carbon nanostructures around it; e – complex 2D nanostructure; f – tree-like carbon nanostructure covered with copper nanoparticles.
The enlarged view of nanostructures reveals their inhomogeneous surface distribution (Fig. 4, b), layered carbon nanostructures (Fig. 4, c), complex 2D nanostructures (Fig. 4, e), and tree-like carbon nanostructures covered with copper nanoparticles (Fig. 4, f). In addition, copper particles with a diameter of 10 μm with a developed system of carbon nanostructures around them were found (Fig. 4, d).

Application perspectives

From a practical point of view, the obtained nanostructures suggest that modified graphite is an excellent source for the production of two-dimensional nanostructures, which can be widely used as components for field-effect transistors, nanofluidic applications, supercapacitors, space technology, and electromagnetic absorbers.

Conclusions

The obtained results allow us to draw certain conclusions about the mechanism of formation of carbon nanostructures on the surface of the modified graphite in an oxygen plasma atmosphere. The presence of a significant number of defects and layered assembly of the source material contributes to the formation of two-dimensional nanostructures, although there is also the emergence of complex petal nanostructures. The processes of formation of such nanostructures can be described by the model of vertical graphite formation, as well as models of growth of one-dimensional structures of copper oxide. This allows us to conclude about the possibility to implement a single theoretical model of the growth of oxide nanostructures of carbon and copper. At the same time, use of noble gases like argon results in exfoliation of the expanded graphite and formation of the layered structures stacked into the tree-like and net-like microstructures composed of the nanolayered graphite 2D structures. The preliminary analysis allows expecting the development of the graphene and the graphene oxide nanostructures in the experiments yet the additional investigations with the transmission electron microscopy (TEM) are necessary.

Acknowledgement. The authors would like to acknowledge financing of National Research Foundation of Ukraine under grant agreement No. 2020.02/0119.

References (GOST 7.1:2006)

References (BSI)


Надійшла до редакції 18.01.2022, розглянута на редколегії 16.02.2022

КАТАЛИТИЧНИЙ СИНТЕЗ НАНОСТРУКТУР ОКСИДУ ГРАФІТА ТА ГРАФІТУ В РЕЖИМІ ПЕРЕХОДУ ВІД ТЛІЮЧОГО ДО ДУГОВОГО ПЛАЗМОВОГО РОЗРЯДУ

А. А. Бреус, С. Л. Абашин, І. М. Луканов, О. Л. Сердюк, О. О. Баранов

Вуглець і матеріали на основі вуглецю, таких як графен і оксид графену, демонструють постійно зростаєчу область застосування в науці, медицині та промисловості. Проте їх реалізації все ще перешкоджає відсутність надійного, гнучкого та високопродуктивного методу синтезу. Більшість існуючих методів засновані на використанні потенційно небезпечних для навколишнього середовища хімічних реагентів. У роботі розроблено фізичний метод, заснований на використанні перехідного тліючого плаズменого розряду, і отримані вуглецеві наноструктури під час одноступійного циклу виробництва в плаズменому реакторі. Існують різні методи виробництва графиту або оксиду графену. Для позбуття росту вуглецевих наносструктур в установці використовується анод з міді, який служить джерелом каталітичних наночастинок міді.

Збільшений вигляд наноструктур показує, що вони являють собою композицію 2D і 1D наноструктур, з'єднаних перемічками, а також наявність деревоподібних і пелюсткових наноструктур з розміром 3 мкм в довжину і 30 нм в діаметрі. Заміна кисню аргоном призвела до істотної зміни зовнішнього вигляду наноструктур. При цьому виявлено шаруваті двовимірні та деревоподібні вуглецеві наноструктури під час одностадійного плаズменного виробництва в установці використовується анод з міді, який служить джерелом каталітичних наночастинок міді.

В результатах за допомогою сканируючої електронної мікроскопії (SEM) на всій поверхні зразка після обробки з'явилося вплив дагового розряду, і отримані вуглецеві наноструктури в ході одностадійного виробництва в плазменному реакторі. Аргон і кисень з'єднані для отримання наноструктур графену або оксиду графену. Для позбуття росту вуглецевих наносструктур в установці використовується анод з міді, який служить джерелом каталітичних наночастинок міді.

Ключові слова: плазма; тліючий розряд; вакуумна дуга; нанотехнології; вуглецеві наноструктури.
углеродные наноструктуры плотностью около 0,01 мкм\(^2\). Увеличенный вид наноструктур показывает, что они представляют собой композицию 2D и 1D наноструктур, соединенных перемычками, а также наличие древовидных и лепестковых наноструктур с размерами около 3 мкм в длину и 30 нм в диаметре. Замена кислорода на аргон привела к существенному изменению внешнего вида наноструктур. При этом обнаружены слоистые двумерные и древовидные углеродные наноструктуры, покрытые частицами меди диаметром до 10 мкм. Полученные наноструктуры позволяют предположить, что модифицированный графит является отличным источником для производства двумерных наноструктур, которые могут быть использованы в качестве компонентов полевых транзисторов, наножидкостных приложений, суперконденсаторов и поглотителей электромагнитных волн.

Ключевые слова: плазма; тлеющий разряд; вакуумная дуга; нанотехнологии; углеродные наноструктуры.

Breeus Andriй Олександрович – канд. техн. наук, доц. каф. теоретичної механіки, машинознавства та роботомеханічних систем, Національний аерокосмічний університет ім. М. Є. Жуковського «Харківський авіаційний інститут», Харків, Україна.

Абашин Сергій Леонідович – канд. фіз.-мат. наук, ст. наук. співроб. наукового відділу каф. космічної техніки та нетрадиційних джерел енергії, Національний аерокосмічний університет ім. М. Є. Жуковського «Харківський авіаційний інститут», Харків, Україна.

Лукашев Іван Миколайович – асистент каф. теоретичної механіки, машинознавства та роботомеханічних систем, Національний аерокосмічний університет ім. М. Є. Жуковського «Харківський авіаційний інститут», Харків, Україна.

Сердюк Олексій Леонідович – аспірант каф. теоретичної механіки, машинознавства та роботомеханічних систем, Національний аерокосмічний університет ім. М. Є. Жуковського «Харківський авіаційний інститут», Харків, Україна.

Баранов Олег Олегович – д-р техн. наук, проф., зав. каф. теоретичної механіки, машинознавства та роботомеханічних систем, Національний аерокосмічний університет ім. М. Є. Жуковського «Харківський авіаційний інститут», Харків, Україна.

Andriй Breus – PhD in Materials Science and Processing Technologies, Associate Professor of Department of Department of Theoretical Mechanics, Engineering and Robomechanical Systems, National Aerospace University "Kharkov Aviation Institute", Kharkov, Ukraine, e-mail: A.Breus@khai.edu.

Sergey Abashin – PhD in Physics of Semiconductors and Dielectrics, Senior Research Fellow of scientific department of the department of space technology and unconventional energy sources, National Aerospace University "Kharkov Aviation Institute", Kharkov, Ukraine, e-mail: S.Abashin@khai.edu.

Ivan Lukashov – Assistant of Department of Theoretical Mechanics, Engineering and Robomechanical Systems, National Aerospace University "Kharkov Aviation Institute", Kharkov, Ukraine, e-mail: Lukashov.Ivan@chdl.de.

Oleksii Serdiuk – PhD Student of Department of Theoretical Mechanics, Engineering and Robomechanical Systems, National Aerospace University "Kharkov Aviation Institute", Kharkov, Ukraine, e-mail: alserdyuk@fed.com.ua.

Oleg Baranov – DSc in Materials Science and Processing Technologies, Professor, Head of Department of Theoretical Mechanics, Engineering and Robomechanical Systems, National Aerospace University "Kharkov Aviation Institute", Kharkov, Ukraine, e-mail: O.Baranov@khai.edu, ORCID: 0000-0001-5356-1125, Scopus Author ID: 7006294413, ResearcherID: I-4066-2018, https://scholar.google.com/citations?user=ZCdsU0cAAAAJ