

Synthesis and characterization of graphene layers from rice husks

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In this work, a method of obtaining graphene layers from natural source specifically from rice husk was developed. A rice husk (RH) was used as a raw material, and potassium hydroxide was used as activation agent. The graphene layers were obtained after four successive stages: pre-carbonization, desilication in 1 M NaOH solution, chemical activation and exfoliation of the carbonized rice husk. The obtained samples were studied using Raman spectroscopy, TEM and SEM; the Raman peaks evidenced the presence of graphene multilayers in the sample. A detailed observation of Raman spectroscopy showed that the obtained samples with ratio of 1/4 and 1/5 (RH/KOH) consisted of graphene layers with a high content of amorphous component. The yield of the product was ~ 3% by weight. This study can provide a new way to the large-scale synthesis of low-cost single and multi-layered graphene using rice husk or other renewable resources.

Keywords: graphene; rice husk; carbonization; exfoliation; chemical activation.

Синтез слоев графена из рисовой шелухи и их характеристики

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В данной работе разработан метод получения слоев графена из природного ресурса. В качестве исходного материала использована рисовая шелуха (РШ), а в качестве активирующего реагента использован гидроксид калия. Слои графена были получены последовательными стадиями: предварительная карбонизация, десиликация в 1 М растворе NaOH, химическая активация и эксфолиация карбонизированной рисовой шелухи. Полученные образцы исследованы с использованием Рамановской спектроскопии, просвечивающей и сканирующей электронной микроскопии. Рамановские пики подтвердили наличие графеновых многослойных слоев в образце. Подробное наблюдение с использованием Рамановской спектроскопии показало, что полученные образцы соотношением 1/4 и 1/5 (РШ/КОН) состоят из графеновых слоев с высоким содержанием аморфного компонента. Выход продукта составлял ~ 3 мас.%. Это исследование может обеспечить новый способ крупномасштабного синтеза однослойного и многослойного графена с использованием рисовой шелухи или других возобновляемых ресурсов.

Ключевые слова: графен; рисовая шелуха; карбонизация; эксфолиация; химическая активация.

Күріш қауызынан графенді синтездеу және олардың сипаттамалары

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Бұл жұмыста табиғи ресурстан графен қабаттарын алу әдісі жасалған. Бастапқы материал ретінде күріш қауызы, ал активтендіруші реагент ретінде калий гидроксиді қолданылған. Графен қабаттары сатылы стадиямен алынған: алдын-ала карбонизациялау, карбонизделген күріш қауызын 1 М NaOH ерітіндісінде десиликациялау, химиялық активациялау және эксфолиациялау. Алынған үлгілер Раман спектроскопия, трансмиссия және сканирлеуші электрондық микроскопия қолданып зерттелінді. Раман спектрлері үлгінің құрамында көп қабатты графеннің бар екенін растады. Раман спектроскопиямен терең зерттеу нәтижесінде, 1/4 және 1/5 (РШ/КОН) қатынасында алынған үлгілер графен қабаттарынан және аморфты көмірден тұратыны анықталды. Өнімнің жалпы шығымы ~ 3 мас.%. Бұл зерттеу жұмысы күріш қауызынан немесе басқа да жаңартылымды ресурстардан бір қабатты және көп қабатты графенді ауқымды синтездеудің жаңа әдісін қамтуы мүмкін.

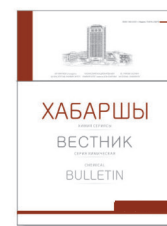
Түйін сөздер: графен; күріш қауызы; карбонизация; эксфолиация; химиялық активация.



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1. Introduction

Graphene is a single layer two-dimensional carbon structure, the surface of which is laid out in regular hexagons with sides of 0.142 nm and carbon atoms at the vertices. Graphene is a semimetal with a small overlap of the conduction and valence bands. Currently, much attention is paid to graphene because of its unusual and potentially useful properties such as high electrical and thermal conductivity, the dependence of electronic properties on the presence of attached radicals of different nature on the surface of graphene, an adjustable band gap, quantum Hall effect, extremely high mobility of charge carriers, high elasticity and good electromechanical characteristics. These properties allow using it in future as the basis for new nanomaterials with improved mechanical, electrical and thermal physical characteristics, as well as an element of nanoelectronic devices [1]. The researches on electronic properties of thin films by Geim and Novoselov have enabled the development of a new stage in the life of graphene [2]. They showed the unique electronic properties of graphene, which gave a new impetus for researchers to further their studies. If in 2007 were published 797 articles devoted to graphenes, in 2008 there were 801 publications, in 2016 their number has already exceeded 1000 titles [3-5].

For several years, since the discovery of the first method for the obtaining of graphene based on the mechanical splitting of graphite layers, the efforts of many research laboratories have been aimed at developing new, more effective approaches to solving this problem. Many methods, such as liquid-phase separation of graphite, its oxidation, graphene synthesis by

chemical vapor deposition, epitaxial growth of graphene on a metal surface, thermal decomposition of carbide, obtaining of graphene in an electric arc, have been used to obtain graphene [3,4]. However, these methods are very time-consuming and have a low yield of graphene. Therefore, the search for new, simpler and cost-effective methods for the synthesis of graphene is an actual task. A promising method can be to obtain graphene layers from agricultural wastes. Agricultural wastes, e.g., rice husks, poplar tree, saxaul, corncob and apricot stones are usually decomposed by burning, which produces ash residues used as sorbents. Among these materials, rice husks have high sorption potential [5] and their stocks are huge in the Republic of Kazakhstan and other countries. Therefore, the obtaining of graphene from rice husks opens the possibility of developing various applications due to its inexpensive, simple and scalable production.

2. Experiment

In this work, rice husk (RH), which is a multi-tonnage and renewable waste was used as a raw material. KOH was used as a typical chemical reagent to induce porosity. This method of obtaining graphene oxide from rice husk was different from the one reported in [6-8]. The carbonized rice husk containing graphene was obtained in four successive stages: pre-carbonization, desilication, activation and exfoliation of the carbonized rice husk (CRH) (Figure 1).

2.1 Pre-carbonization of RH

Firstly, the RH was washed several times with distilled water to remove impurities, and then dried at 110°C for 1 h.

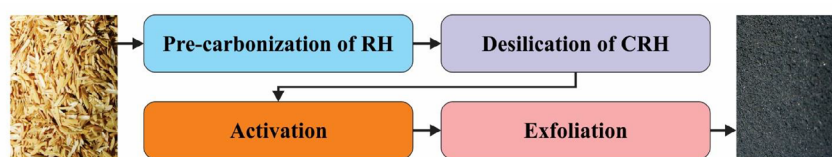


Figure 1 – Illustration of the process of obtaining graphene layers

The pre-carbonization of RH was carried out in a rotating reactor in an inert medium at 250-300°C, with an argon delivery rate of $\sim 5 \text{ cm}^3/\text{min}$, the carbonization time was 45 min [9].

2.2 Desilication of CRH

The resulting samples of CRH (60 g) were desilicated in 3 L of 1 M NaOH solution and heated to 110°C for 3 h to remove SiO_2 , then they were let to settle. The solution was decanted to remove sodium silicate. After that the solution was washed 5-7 times with distilled water (through boiling- sedimentation-decantation) to reach the equilibrium of pH ~ 7 and dried in hot air oven for at least 2 h at 110°C [10].

2.3 Activation

A series of 5 samples of the dried CRH was mixed with crushed KOH at different temperatures and ratios (Table 1). The mixtures were compacted in an iron crucible, and the crucible

was annealed at 850°C for 2 h. To avoid oxidation, argon was supplied at a rate of 5 sccm (standard cubic centimeter per minute). After activation treatment, the resulting samples were washed with distilled water several times to reach the equilibrium of pH ~ 7 , and the filtered samples were dried at 100°C for 24 h. The schematic diagram of self-built carbonization setup is shown in Figure 2.

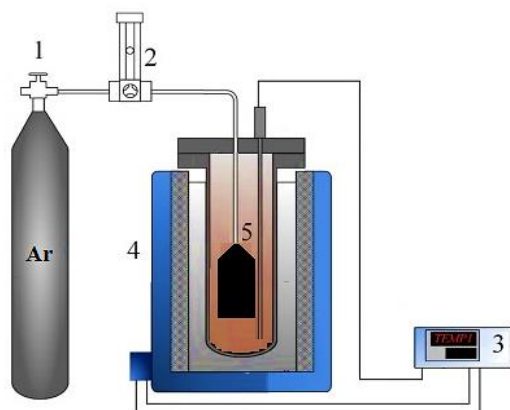
2.4 Exfoliation

The exfoliation process of the CRH was carried out in a solution of hydrogen peroxide (H_2O_2 , 37%) for 48 h, to remove amorphous carbon from the samples. After exfoliation process, the resulting samples were washed and dried with the procedure described above. The yield of the product was $\sim 3\%$ by weight.

3. Results and Discussion

Ko and Day [11] reported the effect of pre-carbonization during the two-stage continuous carbonization process on the final properties of carbon nanomaterials. The progression of pre-carbonization and carbonization were monitored through measurements of density, elemental composition, mechanical properties, and the stacking height of the carbon layer plane. Therefore, we pre-carbonized our RH before carbonization in an inert atmosphere. The surface area of the resulting samples were investigated on the analyzer "Sorbometr M" by low-temperature nitrogen adsorption method (BET-method). The standard calculations of CRH shows that surface area of samples lies from 270 to 350 m^2/g .

In the case of silicon, containing carbon composites the use of alkaline agents such as NaOH or KOH is an extra way to obtain mesoporous materials due to washing out from the matrix the water-soluble Na or K silicates formed by the reaction:

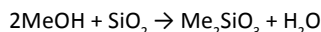


1 – Argon cylinder, 2 – mass flowmeter, 3 – temperature controller, 4 – carbonization reactor, 5 – iron crucible.

Figure 2 – Schematic diagram of self-built carbonization setup

Table 1 – The investigation of optimal ratio and temperature for obtaining graphene layers

Number of sample	Ratio of CRH/KOH, g/g	Temperature, °C	I_G/I_{2D}	I_D/I_G	Number of layers
1	1/4	650	-	-	
2	1/4	750	-	-	
3	1/1.5	850	-	-	
4	1/4	850	2.06	0.29	7 – 8
5	1/5	850	1.57	0.39	4 – 5



where (Me = Na, K), and SiO_2 serves as a template for pore formation. So we used 1 M NaOH solution to obtain porous materials [12].

Potassium hydroxide is a known hygroscopic material letting the carbonization reactions to occur at substantially lower temperatures (its melting point is 380°C) compared to standard pyrolysis which, is governed mostly by radical processes leading in turn to disproportionation reactions yielding tar formation. The purpose of potassium hydroxide is therefore to provide both carbon retention (higher yields, e.g., less amount of volatiles are formed as hydrocarbon tar) and high surface area.

Although the KOH activation is a well-known method to generate the pore network in carbons, the activation mechanism has not been well understood because of the complexity due to the large number of variables in both the experimental parameters and the reactivity of different precursors used. In a general view, the interaction of carbon and KOH starts with solid–solid reactions and then proceeds via solid–liquid reactions including the reduction of potassium (K) compound to form metallic K, the oxidation of carbon to carbon oxide and carbonate, and other reactions among various active intermediates [13].

The real reaction processes and activation mechanisms are variable depending not only on the activation parameters (i.e. amount of KOH, activation temperature, etc.), but also on the reactivity of various carbon sources.

To determine the optimal temperature of the KOH/CRH mixture for obtaining graphene, we took three samples and heated them at 650°C , 750°C and 850°C (Table 1).

We carbonized the rice husks with the addition of KOH in a ratio of 1/1.5 (sample No. 3), 1/4 (sample No. 4) and 1/5 (sample No. 5) at 850°C . Samples obtained at temperatures of 650°C (sample No. 1) and 750°C (sample No. 2) largely retained the amorphous phase of carbon (Figure 3). A sample obtained at 850°C showed the presence of a graphite phase. Calculation data for graphene layers based on Raman spectroscopy indicate a decrease in the number of layers with an increase in the RH/KOH ratio from 1/4 to 1/5.

A quick and accurate way to determine the number of layers of graphene is of a great importance in accelerating the study of this material. As in the previous works [14-15], we determined the number of graphene layers obtained by employing the proposed method.

It is well known, that the typical Raman spectrum of graphene exhibits three peaks: peak D at 1351 cm^{-1} , peak G at 1580 cm^{-1} , and peak 2D at 2700 cm^{-1} . The ratio between the intensities of peak G (I_G) and peak 2D (I_{2D}), I_G/I_{2D} gives an estimate of the number of layers [16]. For monolayer graphene, this ratio is less than unity. The ratio between the intensities of peak D (I_D) and peak G (I_G), I_D/I_G evaluates the defectiveness of graphene layers. Figure 4 shows Raman spectra of graphene layers obtained from CRH (samples No.4 and No.5). The maximum

number of graphene layers is less than ten (Table 1) as indicated by the ratio between the peaks' intensities I_G/I_{2D} . It was shown [17] that the ratio of $I_G/I_{2D} = 1.3$ corresponds to three layers of graphene, whereas the authors of [18] found that $I_G/I_{2D} = 1.8\text{--}2.4$ corresponds to 5-10 layers of graphene.

According to Raman spectra, high-quality graphene multilayer was not found in samples 1, 2, and 3 (Figure 3), in contrast to samples 4 and 5. These results indicate that in our method, a CRH/KOH ratio of 1/4 and 1/5 at 850°C should be used during the preparation.

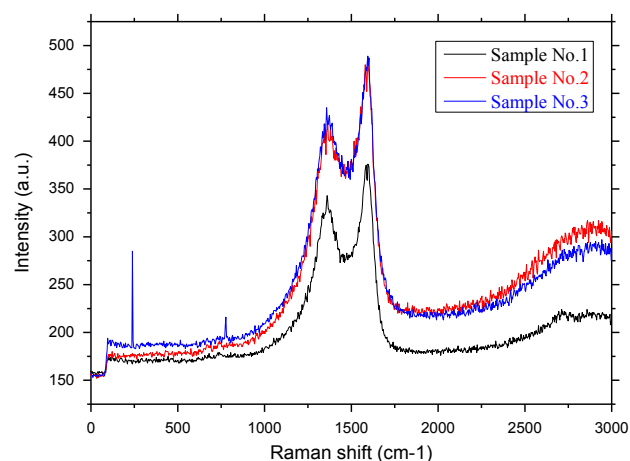


Figure 3 – Raman spectra of samples No. 1, 2 and 3

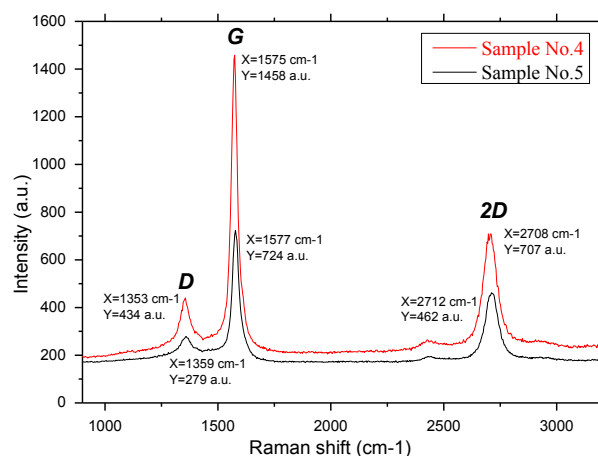


Figure 4 – Raman spectra of sample No.4 and No.5

To identify surface morphological features of synthesized samples, we have used scanning electron microscopy (SEM). Studies were conducted on the microscope Quanta 3D 200i Dual System, FEI. Samples have a complex structure, however, they exhibit a characteristic macrostructure and texture of the surface. Figure 5 shows SEM-images of the samples of synthesized samples.

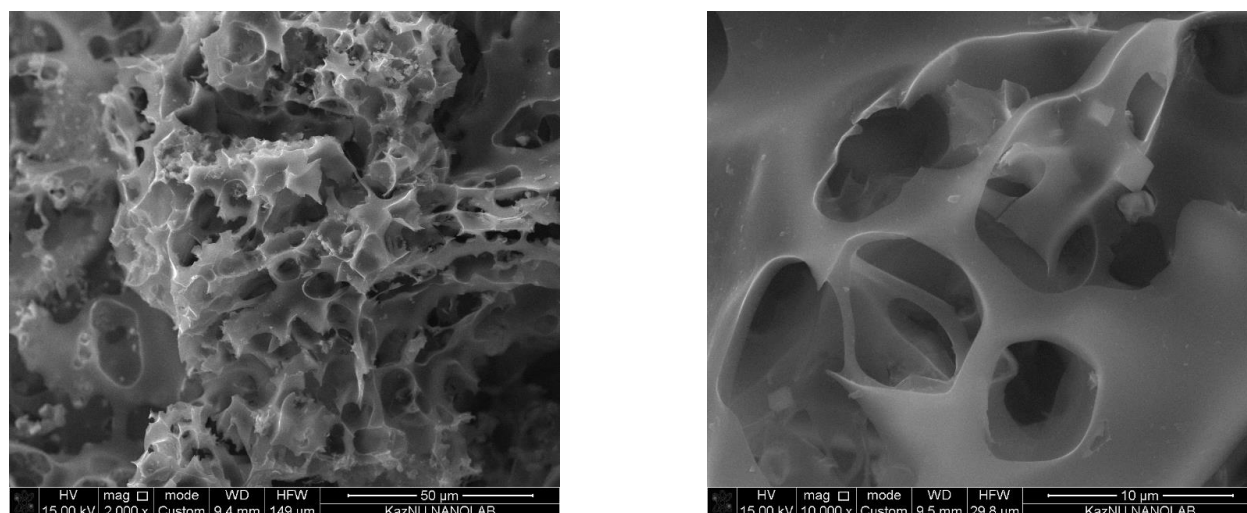


Figure 5 – SEM-images of the CRH

As shown in Figure 5, obtained samples of carbon material have a developed surface, and this method generally does not affect the macrostructure of the samples, which is determined by the original structure of the RH. However, carbonization and chemical activation increase the specific surface of samples, as shown in previous studies [19].

Figure 6 shows the data of elemental analysis of the sample. The sample contains small amounts of silicon (compared to the feedstock). Thus, in the process of desilication, a small amount of silicon (~ 4 wt%) remains in the samples.

Next, the structures of graphene layers were analyzed by transmission electron microscopy (TEM) using a JEM-2100 (JEOL, Japan) instrument with high stability of high voltage and beam current along with an excellent electron-optical system. A TEM image of graphene obtained from CRH by activation with KOH is shown in Figure 7. Samples have defects and inclusions of an amorphous carbon component, but there are sections of layers without defects with a homogeneous surface structure.

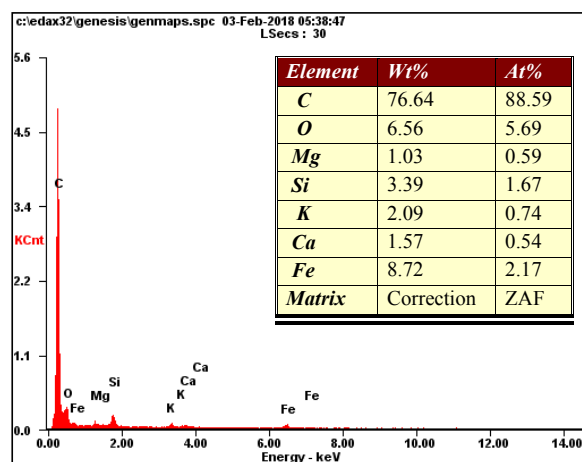


Figure 6 – Elemental composition of the sample No.5

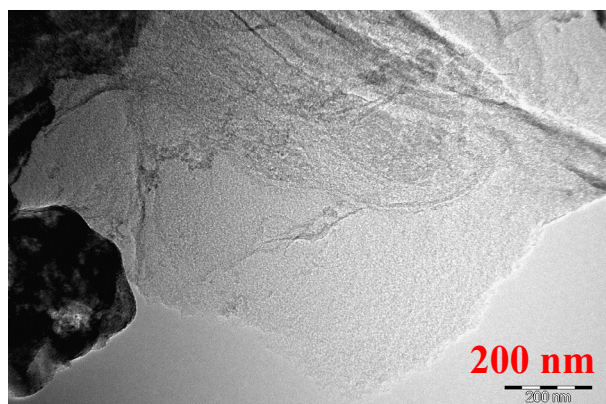


Figure 7 – TEM microimages of the graphene layers

4. Conclusions

A method of obtaining graphene layers from rice husk was developed. Graphene layers were obtained from rice husk by potassium hydroxide activation followed by alkaline desilication. Rice husk samples were subjected to carbonization at the following conditions: 2 h of activation time, 850°C and ratio of rice husk/KOH (wt/wt) was 1/5. Concentration of NaOH desilication solution was 1 M. The obtained samples were studied using Raman spectroscopy, TEM and SEM; the Raman peaks put in evidence the presence of graphene multilayers in the sample. A detailed observation by Raman spectroscopy showed that the obtained samples No. 4 and 5 consisted of graphene layers with a high content of amorphous component. The yield of the product was ~ 3% by weight. Nevertheless, this method appears promising for the production of high quality

graphene layers, since the layers observed in the images of the TEM have an edge structure with domains of several nanometers in addition to topological defects and nanoscale pores. The obtained results show the possibility of obtaining graphene by a simple, cost-effective and scalable method, by carbonization the CRH with KOH.

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