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Vasyl Stefanyk Carpathian National University

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S.A. Lisovska[1,2], N.Ya. Ivanichok[3,4], B. I. Rachiy[1], O.V. Shutak[2], N.R. Ilnytskyi[2], O.I. Bulbuk[2], R.P. Lisovskiy[2, 4]

Investigation of the Nanoporous Structure of Thermally Modified Carbon Materials by Small-Angle X-ray Scatterin

[1]*Vasyl Stefanyk Carpathian National University, Ivano-Frankivsk, Ukraine;*
[2]*Ivano-Frankivsk National Medical University, Ivano-Frankivsk, Ukraine, rlisovsky@ifnmu.edu.ua;*
[3]*G.V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine, Kyiv, Ukraine;*
[4]*Joint Educational and Scientific Laboratory of Gamma Resonance Spectroscopy G.V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine and Vasyl Stefanyk Carpathian National University, Ivano-Frankivsk, Ukraine*

The nanoporous structure of thermally modified carbon materials was studied using the small-angle X-ray scattering (SAXS) method. An analysis of scattering curves in Guinier and Porod coordinates was carried out for the initial and thermally activated materials at 400°C for 30-240 minutes. It was established that thermal treatment for 150-180 minutes promotes the formation of a mesoporous structure with a radius of gyration ranging from 2.69 to 3.53 nm. The application of the Porod method made it possible to assess the fractal morphology of the surface, which varies from smooth to fractal. The obtained results indicate the possibility of controlled regulation of the porosity of carbon materials for sorption and electrochemical applications.

Keywords: nanoporous carbon materials, small-angle X-ray scattering, thermal modification, radius of gyration, Guinier method, Porod method, fractal morphology, mesopores, sorption properties, electrochemical capacitors.

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Introduction

Micro- and mesoporous carbon materials are key for applications in energy storage [1], wastewater treatment [2], gas separation [3], hydrogen storage [4], and catalysis [5]. The efficiency of these materials depends on their developed surface area and controlled nanoporous structure. In addition to the overall surface area, which is determined by macroscopic properties, pore morphology, their size and shape, as well as fractal dimensionality, affect capacitive characteristics [6]. The local pore shape determines the strength of interaction between the carbon material and electrolyte ions, which is important for optimizing the material for a specific electrolyte.

The small-angle X-ray scattering (SAXS) method is an effective tool for analyzing nanostructured materials, particularly for assessing porosity, pore size distribution, fractal structure, and morphological features in the range from a few nanometers to tenths of a micrometer [7, 8]. Combining SAXS with adsorption methods makes it possible to obtain information about closed and open porosity, although the interpretation of SAXS data is complicated by the ambiguity of transformation into a real-space model [9, 10]. The aim of this study is to analyze the nanoporous structure of thermally modified carbon materials using SAXS with Guinier and Porod approximations to evaluate pore sizes and their surface morphology.

I. Materials and methods of research

Nanoporous carbon materials were obtained by the method of thermochemical activation from plant-based raw material [11, 12]. At the first stage, mechanically crushed walnut shells were loaded into an autoclave and heated to 300-350°C at a heating rate of 10°C/min, followed by holding at this temperature for 30 minutes.

The obtained carbonizate was mechanically ground to a fraction of 500 μm and mixed with water and potassium hydroxide in a weight ratio of 1:1:0.5. The resulting mixture was stirred for 30 minutes, then placed in a drying oven and kept at 70-80°C for 48 hours. After complete drying, the obtained material was placed into an autoclave, inserted into a furnace, heated to 900°C at a heating rate of 10°C/min, and held at this temperature for 30 minutes. Cooling was carried out in the switched-off furnace mode. After complete cooling, the carbon material was washed from alkali with distilled water until neutral pH. Thus, a thermochemically activated carbon material of series (L) was obtained. To reveal internal porosity and increase the specific surface area, the obtained carbon material was subjected to additional thermal activation in an oxidative medium (air). Activation was carried out at 400°C for different time intervals from 30 to 240 minutes with a step of 30 minutes. Samples were labeled according to the duration of thermal activation (LH30-LH240).

For the interpretation of SAXS data, various approaches are used, including the Guinier method [13] and the Porod method [14]. The Guinier method is applied to determine the radius of gyration of particles or pores at small scattering angles, which makes it possible to estimate the average size of nanopores or aggregated structures. The Porod method, in turn, makes it possible to analyze surface roughness and the density of phase boundaries, which is important for characterizing porous materials with a developed surface.

Assuming that the pores in the studied carbon materials are homogeneous and limiting the analysis to small values of s, where the scattering intensity does not depend on the internal structure or shape of the carbon particle, the Guinier approximation can be used. At small scattering angles, the Guinier approximation allows describing the dependence of scattering intensity I(s) on the magnitude of the scattering vector s. The Guinier approximation states that at small wave vector values, the scattering profile can be approximated as follows:

$$I(S) = I(0) \cdot e^{\left(-\frac{1}{3}s^2 R_g^2\right)},$$

where *I(S)* is the scattering intensity at a given s, *I(0)* is the intensity in the zero direction ($s = 0$), and *Rg* is the radius of gyration. To determine the radius of gyration, the dependence of ln*(I(s)/I(0))* on s^2 must be obtained. Within the validity of the Guinier approximation, the resulting dependence should have a linear form. The slope of the line allows calculating the radius of gyration.

Analysis of the Guinier curves made it possible to estimate the characteristic sizes of mesopores in the studied carbon materials; however, this approach is effective only in the region of small scattering vectors, where the approximation $s{\cdot}Rg < 1.35$ holds, and the internal structure of the carbon material is not taken into account [13]. For a more complete characterization of the porous structure, in particular for assessing surface roughness, fractal structure, and phase boundary density, the Porod method is appropriate [14].

The Porod method is applied in the region of larges values, where the scattering intensity demonstrates a power-law dependence on the wave vector. This approach allows conclusions to be drawn about the morphology of the porous medium – specifically, the fractal dimensionality of the surface or bulk, as well as the compactness of the nanostructure. Such analysis is especially relevant for nanoporous carbon materials, as their properties, including sorption and electrochemical behavior, are closely related to the geometry of the internal surface [15].

The Porod method is used to analyze the region of large scattering vectors s, where the scattering intensity *I(s)* follows a power-law dependence. For homogeneous systems with a well-defined interfacial boundary, the classical Porod equation establishes a relationship between *I(s)* and s^{-4}. In the case of nanoporous carbon materials, the linear segment on a Porod plot, constructed in the large-s region, not only confirms the presence of clear boundaries between pores and the carbon matrix but also allows assessment of the degree of structural fractality. On a logarithmic scale, the Porod curves are expressed as $\log I(s) = -n \cdot \log s + \log B$, where B is a constant related to the phase contrast and surface area, and n is the slope of the line [14]. The plot of log *I(s)* versus log s in the Porod region should be linear, and the slope of the line allows conclusions about the sample's morphology. If the slope is close to 4, this indicates a smooth porous surface. If the slope is between 3 and 4, it indicates the presence of fractal roughness, i.e., a hierarchical surface structure with nanoscale irregularities, which potentially enhances sorption properties and electrode activity.

II. Results and discussion

The scattering curves obtained for the initial (L) and thermally modified carbon materials (LH30-LH240) are presented in Fig. 1. The graphs show the dependence of relative intensity in a logarithmic scale on the scattering vector s in the range of $s \approx 0.2$-1.6 nm^{-1}. All curves exhibit a similar profile at high s values (s > 0.8 nm^{-1}), which may indicate the preservation of the porous structure. Most changes occur in the low-s region, which corresponds to modifications in the nanoporous structure.

The scattering curve for the initial material (Fig. 1, L) is characterized by an exponential dependence of intensity on the wave vector without pronounced maxima, indicating the absence of a well-defined porous structure or very weak structural ordering. The development of a porous or aggregated structure in the thermally modified materials (Fig. 1, LH30-LH240) is indicated by an increase in relative intensity at low s values. Thermal modification leads to the initiation and development of porosity and changes in fractal dimensionality, as evidenced by changes in the slope of scattering curves for LH60-LH180 materials. With increasing duration of thermal treatment, a gradual increase in intensity at low s is observed for LH30-LH90, suggesting the beginning of pore formation. In the subsequent isothermal holding range (LH120-LH180), scattering intensity further increases at low s, indicating more intensive pore development or changes in aggregate size. For LH210-LH240, the intensity reaches a maximum and then decreases compared to previous samples, which may indicate pore wall collapse and merging, resulting in structural stabilization and mesopore development due to prolonged thermal exposure.

It should be noted that differences in the intensity curves are observed only at low *s* values, indicating changes in the porous structure of the material. Some samples also exhibit minor inflections or local features, which can be interpreted as the emergence of specific pore sizes or intermolecular distances. Thermal treatment significantly affects the structure of carbon materials. The optimal thermal treatment time for porosity development is likely in the range of 120-180 minutes, after which structural degradation or stabilization may begin. SAXS results confirm data obtained from low-temperature porometry regarding the formation of meso- or macroporous structures following thermal modification.

The Guinier curves for the initial sample (L) and thermally activated carbon materials (LH30-LH240) are shown in Fig. 2. All curves demonstrate linear regions in the coordinates *ln(I(s)/I(0))* versus s^2, confirming the applicability of the Guinier approximation and allowing accurate estimation of the radius of gyration *(Rg)* of the porous structures. For correct *Rg* evaluation, the Guinier approximation was applied in the region $s_{min} \cdot Rg > 0.1$ and $s_{max} \cdot Rg < 1.35$, with a measurement error of 10 %.

The calculated *Rg* values are presented in Table 1. For the initial sample L, *Rg* is 2.69 nm, indicating the initial presence of a fine porous structure. After thermal activation for 30 minutes (LH30), the radius of gyration slightly increases to 2.81 nm, which may be associated

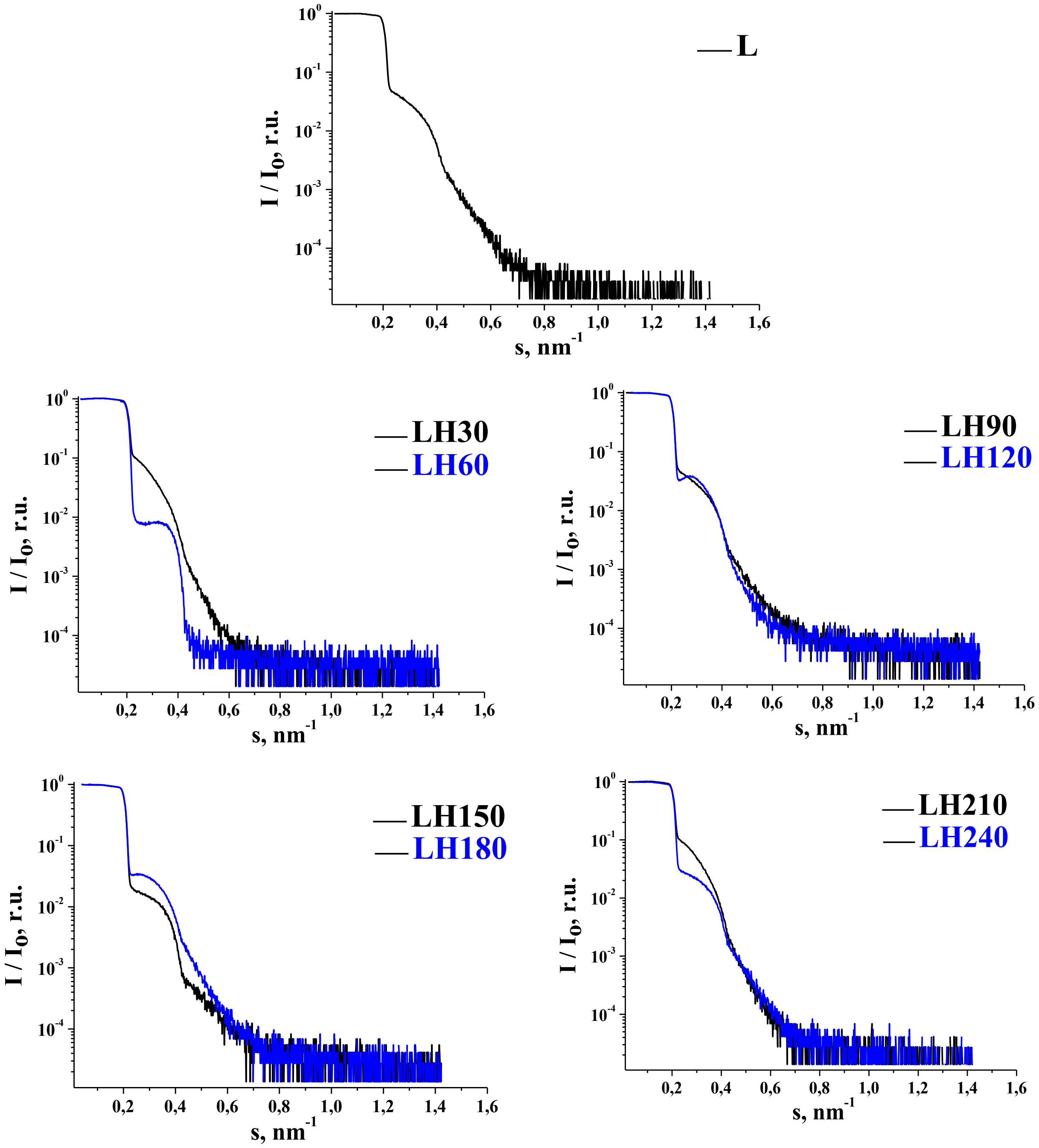

Fig. 1. Relative intensity curves of small-angle X-ray scattering for the initial (L) and thermally modified carbon materials (LH30-LH240).

with partial opening of closed pores.

The most significant changes are observed during activation for 150-240 minutes. The *Rg* value for LH150 is 3.53 nm, and for LH240 it is 3.39 nm, indicating noticeable enlargement of nanoporous domains or partial merging of smaller pores into larger ones. This is consistent with the hypothesis that prolonged activation in an air atmosphere may cause surface carbon burn-off, opening or expanding existing pores. It should be noted that after reaching the maximum (LH150), *Rg* slightly decreases in LH180 and LH210 samples, possibly due to partial structural degradation or pore recombination. However, with further increase in duration (LH240), *Rg* rises again to 3.39 nm, suggesting the final phase of mesoporous structure stabilization.

For a clearer understanding of the physical pore sizes in nanoporous carbon materials, the calculated radii of gyration *(Rg)* from the Guinier curves were used to estimate the effective pore radius *(Rp)* [13]. For this purpose, a model was applied in which pores are approximated as spherical. It is known that for a homogeneous sphere, the radius of gyration is related to its geometric radius by the following relationship: $R_g = \sqrt{\frac{3}{5}} \cdot R_p$. Thus, the calculated *Rp* values can be considered as an estimate of the average pore size within the assumed spherical morphology. The results are presented in Figure 3 and were used for further interpretation of changes in the porous structure due to thermal activation.

The results indicate that thermal activation significantly affects the nanoporous structure of carbon materials. The largest increase in pore radius is observed after 150 minutes of thermal treatment at 400 °C. This suggests optimal activation conditions for forming a well-developed porous structure suitable for adsorption applications or as a base for electrode materials in electrochemical capacitors.

The X-ray scattering curves plotted in Porod coordinates for the initial (L) and thermally activated carbon materials (LH30-LH240) are shown in Figure 4. The Porod approximation was applied for scattering vector values satisfying $s > 1/Rg$, limited to the region where noise is present.

The curves (Fig. 4) exhibit linear regions, from which the slope of the line was calculated (Table 2). From these results, it can be inferred that carbon materials LH30 and LH210 have $n \approx 4$, indicating smooth phase boundaries and classical surface scattering according to Porod. Materials with $n < 3$ (LH60, LH120, LH150, LH180)

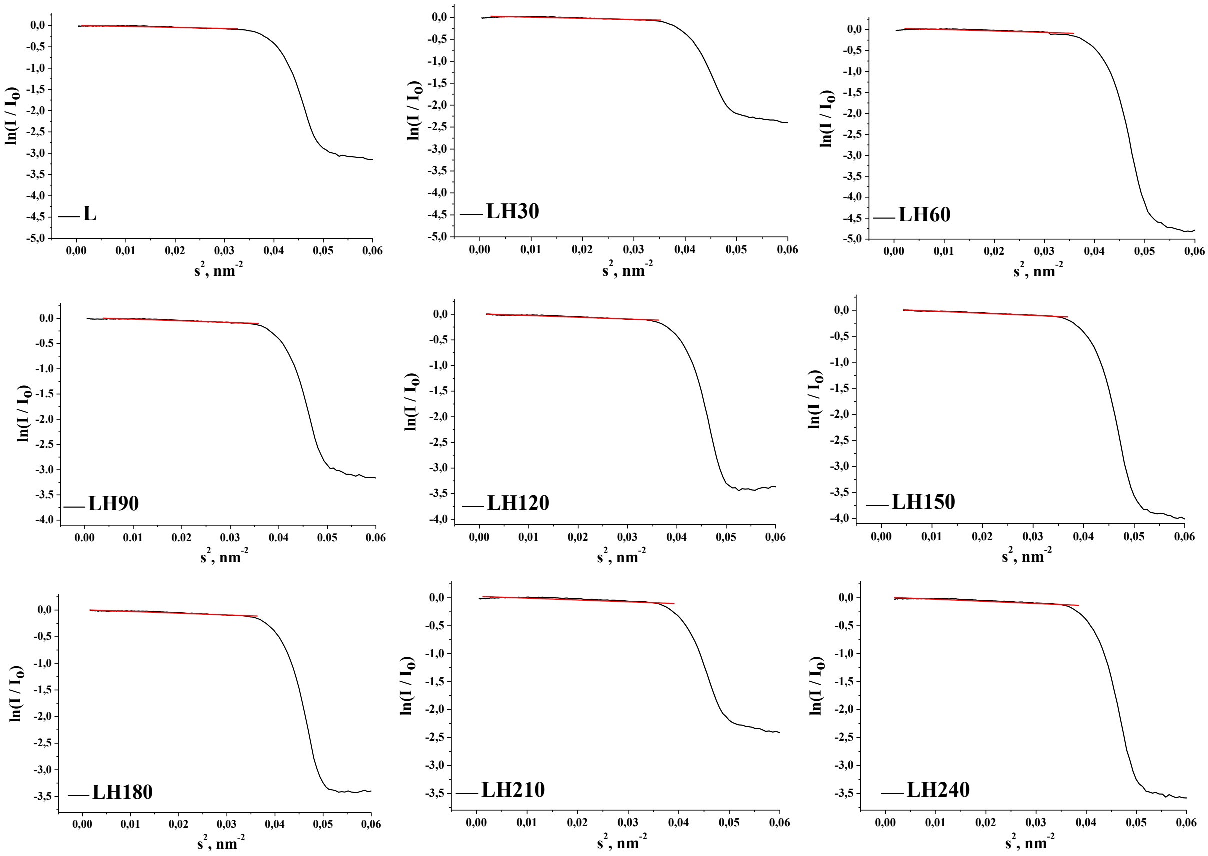

Fig. 2. X-ray scattering curves in Guinier coordinates and their approximations for the initial (L) and thermally modified carbon materials (LH30-LH240).

Table 1.

Radius of gyration calculated from SAXS curves for the initial (L) and thermally modified carbon materials (LH30-LH240).

Sample	L	LH30	LH60	LH90	LH120	LH150	LH180	LH210	LH240
Rg, nm	2.69	2.81	3.24	3.15	3.20	3.53	3.13	3.14	3.39

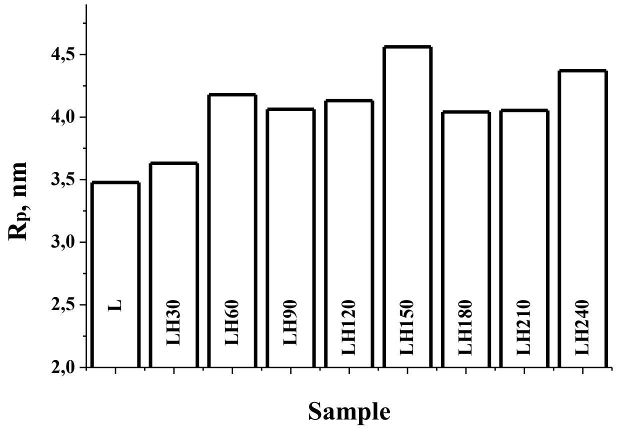

Fig. 3. Pore radius calculated from SAXS curves for the initial (L) and thermally modified carbon materials (LH30-LH240).

exhibit fractal surface morphology or volumetric heterogeneity, characteristic of more porous or less ordered structures. Materials (L, LH90, LH240) with Porod indices in the range $3 < n < 4$ display surface fractality, corresponding to an uneven but not chaotic morphology.

For all carbon materials, the Porod index varies between 2.4-4.1, indicating that structural properties depend on the degree of sample activation. Periodic alternation of smooth and fractal characteristics is observed, which may be related to the mechanism of pore formation during thermal treatment.

Conclusions

The nanoporous structure of thermally activated carbon materials, synthesized with varying thermal treatment durations, was investigated using SAXS.

Analysis of the curves in Guinier coordinates allowed determination of the samples' radii of gyration, which range from approximately 2.7 to 3.5 nm. With increasing thermal treatment duration (up to 150 min), there is a trend of increasing radius of gyration, indicating the formation of a mesoporous structure.

Plotting lines in Porod coordinates and determining the slope enabled evaluation of the surface character and pore interface – from smooth (for $n \approx 4$) to fractal or diffuse (for $n < 4$). Samples with maximum n values (~4.1 for LH30, ~4.0 for LH210) exhibit a characteristic smooth pore boundary, whereas other samples (e.g., LH60, LH180) have $n \approx 2.4$, indicating a more diffuse or

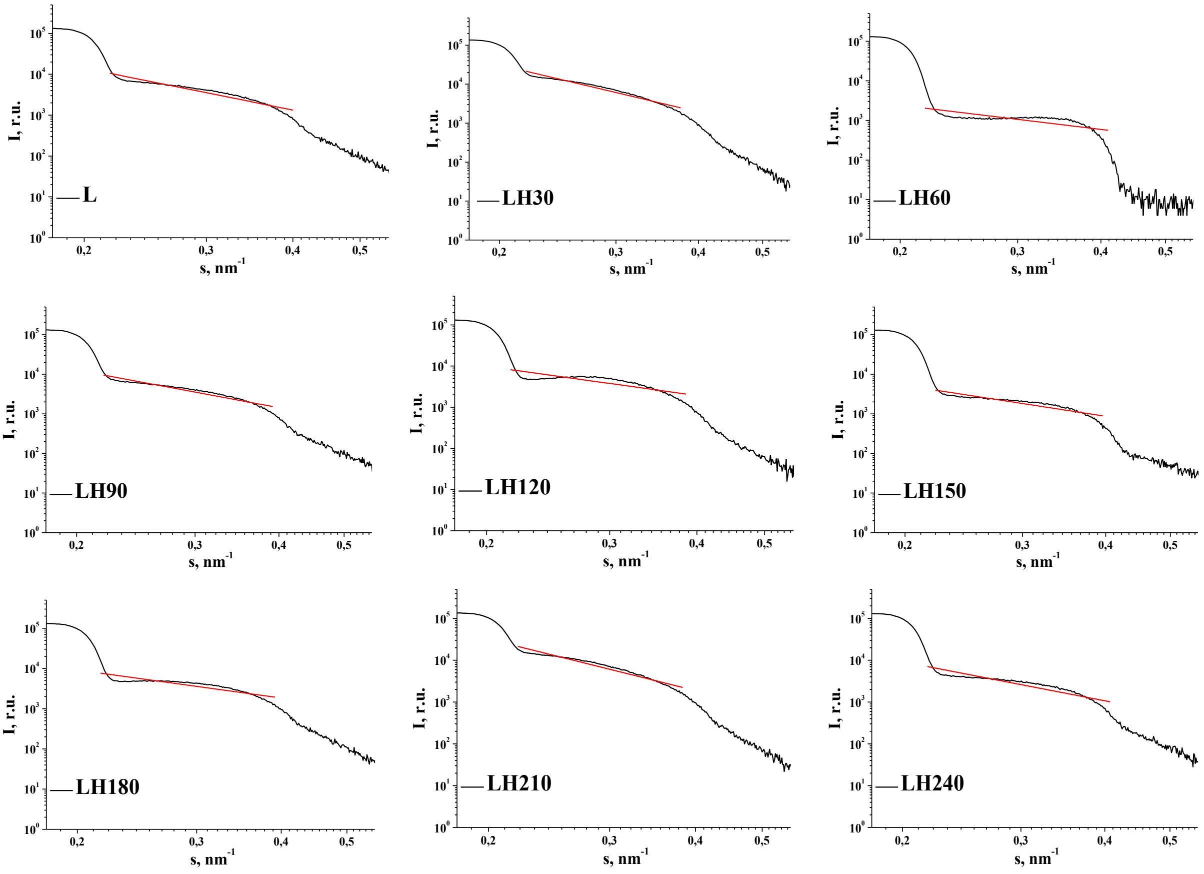

Fig. 4. X-ray scattering curves in Porod coordinates and their approximations for the initial (L) and thermally modified carbon materials (LH30-LH240).

Table 2.

Porod coefficient calculated from SAXS curves for the initial (L) and thermally modified carbon materials (LH30-LH240).

Sample	L	LH30	LH60	LH90	LH120	LH150	LH180	LH210	LH240
n	3.3	4.1	2.4	3.4	2.7	2.6	2.4	4.0	3.3

hierarchical surface structure.

The combined analysis using Guinier and Porod approximations allowed characterization not only of pore size but also of the type of pore surface, which is important for the subsequent use of these materials as electrodes or sorbents. It was established that structural parameters, including the radius of gyration and Porod exponent, show a complex dependence on thermal treatment conditions. This demonstrates the possibility of controlled regulation of the materials' morphological characteristics by adjusting the duration of thermal processing.

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Lisovska S.A. – Ph.D., Lecturer of the Professional Medical College of Ivano-Frankivsk National Medical University;
Ivanichok N.Ya. – Leading specialist of Joint Educational and Scientific Laboratory for Physics of Magnetic Films;
Rachiy B. I. – Dr. Sci., Professor of the Department of Applied Physics and Materials Science;
Shutak O.V. – Ph.D., Associate Professor of the Department of Orthopedic Dentistry, Ivano-Frankivsk National Medical University;
Ilnytskyi N.R. – student of the Ivano-Frankivsk National Medical University
Bulbuk O.I. – Ph.D., Vice-Rector Ivano-Frankivsk National Medical University;
Lisovskiy R.P. – Dr. Sci., Professor of the Department of Medical Informatics, Medical and Biological Physics, Ivano-Frankivsk National Medical University, leading specialist of Joint Educational and Scientific Laboratory.

[1] G. Chen, Z. Hu, Z. Pan, D. Wang. *Design of honeycomb-like hierarchically porous carbons with engineered mesoporosity for aqueous zinc-ion hybrid supercapacitors applications*. Journal of Energy Storage, 38, 102534 (2021); https://doi.org/10.1016/j.est.2021.102534.

[2] M.S. Soffian, F.Z.A. Halim, F. Aziz, M.A. Rahman, M.A. Mohamed Amin, D.N.A. Chee. *Carbon-based material derived from biomass waste for wastewater treatment*. Environmental Advances, 9, 100259 (2022); https://doi.org/10.1016/j.envadv.2022.100259.

[3] P. Zhang, J. Wang, W. Fan, Y. Zhong, Y. Zhang, Q. Deng, Z. Zeng, S. Deng. *Ultramicroporous carbons with extremely narrow pore size distribution via in-situ ionic activation for efficient gas-mixture separation*. Chemical Engineering Journal, 375, 121931 (2019); https://doi.org/10.1016/j.cej.2019.121931.

[4] S. Stock, N. Kostoglou, J. Selinger, S. Spirk, C. Tampaxis, G. Charalambopoulou, T. Steriotis, C. Rebholz, C. Mitterer, O. Paris. *Coffee Waste-Derived Nanoporous Carbons for Hydrogen Storage*. ACS Applied Energy Materials, 5(9), 10915 (2022); https://doi.org/10.1021/acsaem.2c01573.

[5] I. Matos, M. Bernardo, I. Fonseca. *Porous carbon: A versatile material for catalysis*. Catalysis Today, 285, 194 (2017); https://doi.org/10.1016/j.cattod.2017.01.039.

[6] B. Yan, J. Zheng, L. Feng, Q. Zhang, C. Zhang, Y. Ding, J. Han, S. Jiang, S. He. *Pore engineering: Structure-capacitance correlations for biomass-derived porous carbon materials*. Materials & Design, 229, 111904 (2023); https://doi.org/10.1016/j.matdes.2023.111904.

[7] D. Saurel, J. Segalini, M. Jauregui, A. Pendashteh, B. Daffos, P. Simon, M. Casas-Cabanas. *A SAXS outlook on disordered carbonaceous materials for electrochemical energy storage*. Energy Storage Materials, 21, 162 (2019); https://doi.org/10.1016/j.ensm.2019.05.007.

[8] C.J. Jafta, A. Petzold, S. Risse, D. Clemens, D. Wallacher, G. Goerigk, M. Ballauff. *Correlating pore size and shape to local disorder in microporous carbon*. Carbon, 123, 440 (2017); https://doi.org/10.1016/j.carbon.2017.07.046.

[9] C. Prehal, C. Koczwara, N. Jäckel, H. Amenitsch, V. Presser, O. Paris. *A carbon nanopore model to quantify structure and kinetics of ion electrosorption with in situ small-angle X-ray scattering*. Physical Chemistry Chemical Physics, 19(23), 15549 (2017); https://doi.org/10.1039/c7cp00736a.

[10] C. Prehal, S. Grätz, B. Krüner, M. Thommes, L. Borchardt, V. Presser, O. Paris. *Comparing pore structure models of nanoporous carbons obtained from small angle X-ray scattering and gas adsorption*. Carbon, 152, 416 (2019); https://doi.org/10.1016/j.carbon.2019.06.008.

[11] S.A. Lisovska, R.V. Ilnytskyy, R.P. Lisovskyy, N.Ya. Ivanichok, Kh.V. Bandura, B.I. Rachiy. *Structural and sorption properties of nanoporous carbon materials obtained from walnut shells*. Physics and Chemistry of Solid State, 24 (2), 348 (2023); https://doi.org/10.15330/PCSS.24.2.348-353.

[12] B.K. Ostafiychuk, N.Ya. Ivanichok, S-V.S. Sklepova, O.M. Ivanichok, V.O. Kotsyubynsky, P.I. Kolkovskyy, I.M. Budzulyak, R.P. Lisovskiy. *Influence of plant biomass activation conditions on the structure and electrochemical properties of nanoporous carbon material*. Materials Today: Proceedings, 62(9), 5712 (2022); https://doi.org/10.1016/j.matpr.2022.01.486.

[13] C.D. Putnam. *Guinier peak analysis for visual and automated inspection of small-angle X-ray scattering data*. Journal of Applied Crystallography, 49(5), 1412 (2016); https://doi.org/10.1107/S1600576716010906.

[14] B.K. Ostafiychuk, et al. *SAXS investigation of nanoporous structure of thermal-modified carbon materials*. Nanoscale Research Letters, 9, 160 (2014); https://doi.org/10.1186/1556-276X-9-160.

[15] Y. Starchuk, N. Ivanichok, I. Budzulyak, S. Sklepova, O. Popovych, P. Kolkovskyi, B. Rachiy. *Electrochemical properties of nanoporous carbon material subjected to multiple chemical activation*. Fullerenes, Nanotubes and Carbon Nanostructures, 30(9), 936 (2022); https://doi.org/10.1080/1536383X.2022.2043285.

С.А. Лісовська[1,2], Н.Я. Іванічок[3,4], Б.І. Рачій[1], О.В. Шутак[2], Н.Р. Ільницький[2],
О.І. Бульбук[2], Р.П. Лісовський[2,4]

Дослідження нанопористої структури термічно модифікованих вуглецевих матеріалів методом малокутового Х-променевого розсіяння

[1]*Карпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна*
[2]*Івано-Франківський національний медичний університет, Івано-Франківськ, Україна, rlisovsky@ifnmu.edu.ua*
[3]*Інститут металофізики імені Г.В. Курдюмова НАН України, Київ, Україна*
[4]*Спільна навчально-наукова лабораторія гамма-резонансної спектроскопії Інституту металофізики ім. Г.В. Курдюмова НАН України та Карпатського національного університету імені Василя Стефаника, Івано-Франківськ, Україна*

Досліджено нанопористу структуру термічно модифікованих вуглецевих матеріалів методом малокутового Х-променевого розсіяння (SAXS). Проведено аналіз кривих розсіяння у координатах Гіньє та Порода для вихідного та термічно активованих матеріалів при 400 °C протягом 30–240 хвилин. Встановлено, що термічна обробка протягом 150–180 хвилин сприяє формуванню мезопористої структури з радіусом гірації від 2,69 до 3,53 нм. Застосування методу Порода дозволило оцінити фрактальну морфологію поверхні, яка варіюється від гладкої до фрактальної. Отримані результати свідчать про можливість контрольованого регулювання пористості вуглецевих матеріалів для сорбційних та електрохімічних застосувань.

Ключові слова: нанопористі вуглецеві матеріали, малокутове Х-променеве розсіяння, термічна модифікація, радіус гірації, метод Гіньє, метод Порода, фрактальна морфологія, мезопори, сорбційні властивості, електрохімічні конденсатори.