

Micro-and Mesoporous Carbon Inverse Opal Nanostructures

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Abstract — The formation of the porous system in carbon inverse opal (C-IOP) nanostructures has been studied. The synthesis of C – IOP was performed using opal matrix as the template and sucrose as the carbon source. Activation of the samples was carried out using potassium hydroxide. Characteristics of the porous structure were determined by gas adsorption - desorption. The morphology and structure of the samples was investigated by high-resolution transmission electron microscopy (HRTEM).

I. INTRODUCTION

Nanostructured carbon materials are widely used in many fields of technology. The most active development areas related to portable power source in microelectronics, energy storage, the components of the power pulse devices, and other devices, where there is a need a fast source of energy [1].

The most important parameters of carbon materials used in electrochemical power sources as electrodes, are the specific surface area, pore size and topology. The high specific surface area increases the ability of carbon to accumulate charges on its surface. The main contribution to the specific surface area makes the micropores (diameter less than 2 nm) [2]. The presence of mesopores (diameter from 2 to 50 nm) inside the electrode material is extremely important for rapid transport of ions. Interconnected system of micro - and mesopores in combination with the high surface area of the electrodes increases the output characteristics of devices [3].

There are of some carbon nanostructures, for example, molecular sieves [4], obtained by carbonization of organic compounds in mesoporous silica, and carbon structure with three-dimensional periodicity, based on the opal template [5]. A number of mesostructured silica matrices, such as MCM48, MCM41, SBA15, impregnated with carbon precursors (sugar solution, propylene, resin, etc.), carbonized and removed of SiO₂ by dissolving in a solution of hydrofluoric acid [2, 6-8].

In this work the influence of thermo-chemical treatment of opal matrices impregnated with carbon-containing compounds, followed by the removal of silicon dioxide on the formation a porous structure. The particle sizes of the silica particles ranged from 10 to 300 nm. Characteristics of the porous structure were determined by gas adsorption-desorption. The morphology and structure of the samples were investigated by HRTEM.

II. EXPERIMENTAL

The synthesis of C – IOP was performed using opal matrix as the template and sucrose as the carbon source. Opal matrices have been prepared by

sedimentation of suspensions of monodisperse colloidal silica particles. The technique of preparation of the opal matrices is detailed in [9]. The silicon dioxide particles were obtained by direct hydrolysis of tetraethoxysilane (TEOS) in alcohol-water-ammonia solution. Colloidal particles of small size (10 -12 nm) were synthesized by hydrolysis of TEOS in the presence of L-arginine [10] and precipitated by centrifugation. It should be noted that after the centrifugation a disordered matrix was formed with colloidal SiO₂ particles. Under carbonization inside the pores the carbon does not form of inverse opal matrix and can create a variety of structural motifs depending on the heat treatment.

An aqueous solution of sucrose C₁₂H₂₂O₁₁ with the addition of sulfuric acid has been impregnated inside the opal matrix. The resulting carbon-containing matrix has been activated by alkali KOH at 1070K in an inert atmosphere, 2 h.

Adsorption-desorption isotherms of nitrogen were recorded at 77 K (device Quantachrome QuadraWin), from which the characteristics of the porous system were derived. Terms preliminary of the sample degassing were: 300 ° C, 2 h, He. The morphology and microstructure of the samples were studied by a transmission electron microscope of JEM-2100.

III. RESULTS AND DISCUSSIONS

Terms of thermochemical treatment (TChT) and the parameters of the porous system of the samples measured are listed in Table 1.

The samples were designated conditionally as SiC / C - IOP (act.): it is of SiC / C inverse opal composite (IOP), activated by potassium hydroxide, C-IOP (act.): it is of carbon inverse opal nanostructure, activated by potassium hydroxide, and C - disord. (act.): it is of carbon nanostructure with a disordered lattice, activated by potassium hydroxide.

SiC / C-IOP samples are formed at high-temperature TChT (1770K), when a silicon carbide is synthesized by carbothermic reduction of SiO₂ partly [11]. C-IOP samples were heat-treated at 1200K, when

SiC formation does not occur. Samples in the table 1 without «act.» have been not subjected of the alkaline activation.

Comparison of the results shows a clear dependence of the porosity on the diameter of the silica particles and the temperature of carbonization. Alkaline activation changes also significantly of the porous structure. So, the activation of number 4 sample leads to an increase of specific surface area and pore volume of

2.5 times compared with the number 3 sample, for which the activation was not carried out.

Fig. 1 shows the adsorption-desorption isotherms of nitrogen for the three samples. Isotherm (1) refers to the SiC/C –IOP act. composite (sample number 2, table 1). The sample was subjected by thermochemical treatment at 1770 K, 2 h, in a vacuum with subsequent activation of potassium hydroxide at 1070 K.

TABLE 1. TERMS OF THERMOCHEMICAL TREATMENT AND PARAMETERS OF THE POROUS SYSTEM FOR THE SAMPLES MEASURED.

Number	Samples	SiO ₂ diam., nm	TChT, K	Specific surface area ¹ , m ² /g	Total pore volume ² , cm ³ /g	Micropore volume ³ , cm ³ /g	Pore size ⁴ , nm
	SiC/C –IOP	300	1770	180	0.57	0.045	1.0; 3.3; 5.5; 8.8
	SiC/C –IOP act.	300	1770	294	0.51	0.09	0.7; 1.5; 2.5; 3.3; 5.7; 8.2
	C –IOP	300	1200	570	0.70	0.21	0.7; 3.0; 5.7; 8.8
	C –IOP act.	300	1200	1448	1.72	0.51	0.7; 1.5; 3.0; 5.7; 8.0
	SiC/C –IOP act.	73	1770	2.65	-	-	1.9
	C –IOP	73	1200	430	0.75	0.15	0.7; 3.1; 11.7
	C –disord. act.	12	900	2050	0.99	0.81	0.8;1.2; 1.4; 1.8; 3.1
	C –disord. act.	10	900	2478	1.56	0.92	0.8; 1.4; 3.0;

¹ - specific surface area calculated by the BET method in the pressure range of 0.05 - 0.20

² - total pore volume is calculated by volume of nitrogen adsorbed at P / Po = 0.99

^{3,4} - the micropore volume (<2 nm) and the most notable pore size have been calculated by DFT in the model slit pore QSDFT (Quenched solid density functional theory). Error in the fit is 0.3-0.7% for different isotherms

Isotherm (2) refers to the C –IOP act. (sample number 4, Table 1).

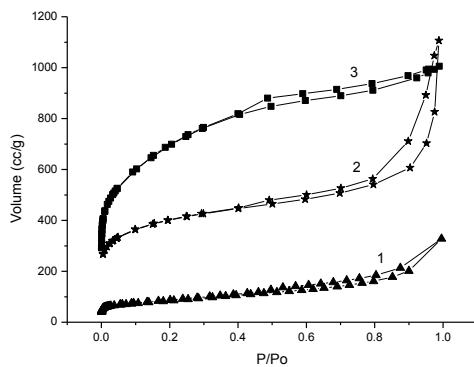


Fig. 1. Adsorption - desorption isotherms (77 K) of nitrogen by carbon nanostructures based on inverse opal: 1 - sample number 2, 2 - sample № 4, 3 - sample number 8. Sample numbers correspond to Table 1.

The sample was subjected by thermochemical treatment at 1200 K, 2 h, in a vacuum with subsequent activation of potassium hydroxide at 1070 K. Isotherm (3) refers to the C –disord. act. nanostructure, activated by potassium hydroxide (sample number 8, Table 1). The sample was subjected by thermochemical treatment at 900 K, 2 h, in a vacuum with subsequent activation of potassium hydroxide at 1070K.

Isotherms are of type II according to [12], which corresponds to polymolecular adsorption. Sorption hysteresis loop is close to the point of relative pressure P / Po = 0.4, indicating a predominance of micropores (less than 2 nm). The dominant contribution of micropores to the surface area shows the proportional relationship between the micropore volume and surface area (by BET). Micropore volume in this series of samples has increased by 20 times, the surface area increased 14 times and total pore volume growth was only 3 times. It should be noted that the proportional relationship between the micropore volume and surface area is observed for all

sizes of silica particles of opal matrices used in this work. Pore size distribution and their contribution to the pore volume also show a major impact of the micropores on the surface area. Fig. 2 shows the curves of the pore size distribution for the samples № 2, № 4 and № 8 and appropriate volumes accumulated in these pores.

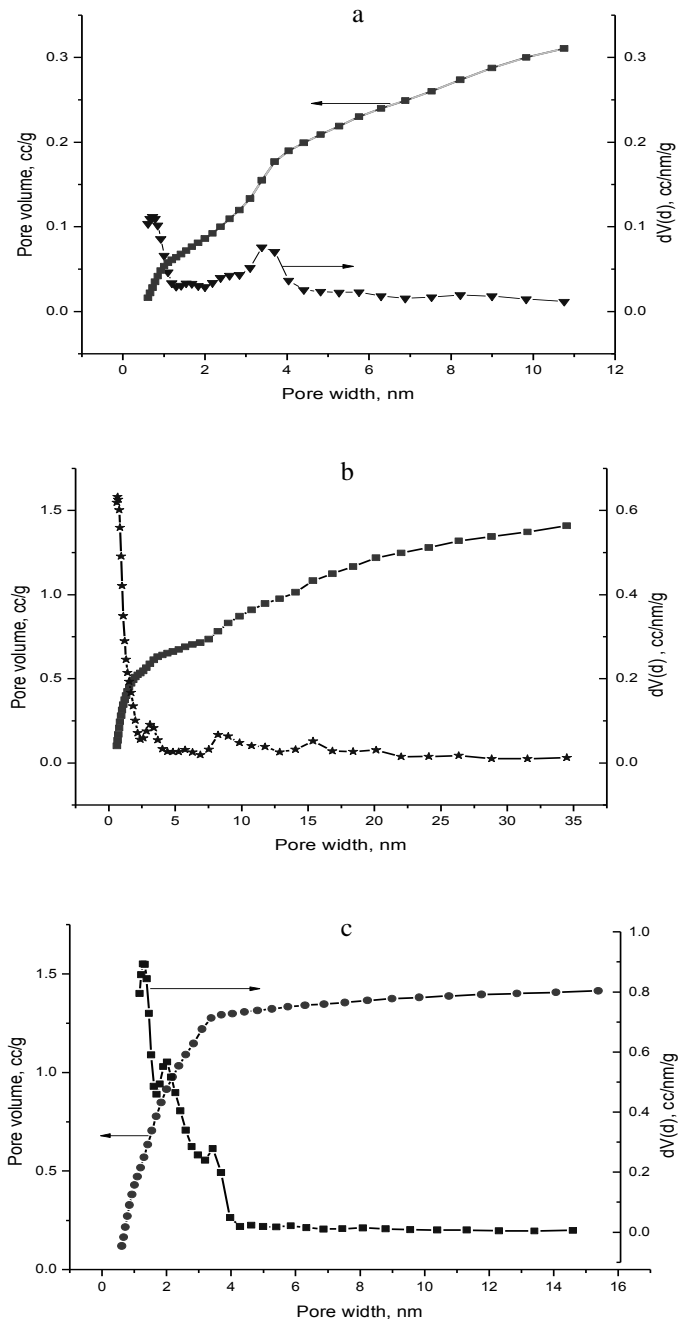


Fig. 2. Pore size distribution for samples number 2 (a), 4 (b) and 8 (c) and volume accumulated in these pores.

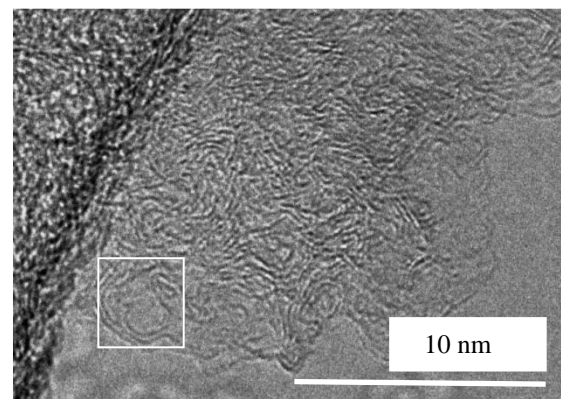
The graphs clearly show that the curve of the volume change is rising steeply for the sample number 8 (area 2478 m² / g) only in the micropore range and it reaches a plateau when pore size is more than 3 nm. The volume change curves for samples with a smaller surface area (number 2 and number 4, Fig. 2a, b) have a small steep

part for micropore range and the curves gradually rises before reaching a plateau in the mesopore range. This behavior indicates on the mesopore existence with a broad size distribution. Indeed, the sample number 2 (Fig. 3a) and number 4 (Fig. 2b) show of the pore sizes up to 20 nm with a wide distribution (in size) around each peak. Sample № 8 shows of mesopores only one size of 3 nm (Fig. 2c), and the sample number 7 does not show of isolated mesopores and the proportion of micropores in the total pore volume is 82%.

Activation promotes increase of the pore volume and the formation of micropores. Analysis of experimental data shows that during the activation micropore volume and total pore volume were increased proportionally each other for the samples treated at 1200K and 900K. This relationship is not always observed for samples heat-treated at 1770K. Alkali treatment significantly developed of 0.7 nm micropores and 3 nm mesopores.

Among emerging micropores it should be allocated of the pores of 1.4 nm in size, which are formed in all samples, regardless of the treatment temperature and the particle size of silica. Potassium hydroxide also promotes the development of 1.2 nm and 1.8 nm micropores (sample 7, Table 1).

Concluding of carbon structure characterization by gas adsorption - desorption it should be allocated among the many factors affecting the principal that, namely, the treatment temperature and silica particle size in the initial opal matrix. These two parameters have a decisive influence on the formation and development of the porous structure. Besides them the alkaline activation is essential for the development of a microporous structure. Only after activation the samples show the maximum surface area (up to 2500 m² / g) and the maximum pore volume (up to 1.72 cm³ / g). HRTEM study of the samples has showed that the structure of SiC / C composite (sample 1, Table 1) consists of SiC crystallites, graphite, amorphous carbon and spherical carbon particles containing concentric graphite shells (onion-like). For samples treated at 1200K, bulbous particles are almost spherical in shape, but poorly organized nanostructure with a small number of



carbon layers.

Fig. 3 HRTEM image of the onion-like particle with hollow core of 1.5 nm in size.

Fig. 3 shows the image of an area of the sample 4, where a particle with three graphite-like layers in a shell and empty core of 1.5 nm in diameter was selected by frame. Known mechanisms of onion-particle synthesis cannot explain of them formation in our experiments. Elucidation of the mechanism requires further investigation.

IV. CONCLUSION

The influence of thermo-chemical treatment of opal matrices impregnated with carbon-containing compounds followed by the removal of silicon dioxide on the formation a porous structure has been studied. It is shown that the temperature of sample treatment and particle size of the silica in the initial opal matrix have a decisive influence on the formation and development of the porous structure. The alkaline activation is essential for the development of a microporous structure. Only after activation the samples show the maximum surface area (up to 2500 m² / g) and the maximum pore volume (up to 1.72 cm³ / g).

Onion-like carbon nanoparticles formed during high-temperature treatment of samples were detected by HRTEM method. The mechanism of them formation is not defined. It is suggested that the sorption pores ~ 1.5 nm can be attributed to voids observed in the cores of onion-shaped nanoparticles. Carbon nanostructures with high surface area are promising materials as sorbents, sensors, catalysts, and electrodes.

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