Synthesis and Study of the Properties of Porous Carbon–Carbon Nanocomposites with Nitrogen-Containing Carbon Nanofibers

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Abstract—The possibility of synthesizing carbon–carbon nanocomposites with nanofibers embedded in a carbon matrix by two-stage dehydrochlorination (under the action of alkali followed by carbonization) of a carbon-chain chloropolymer has been shown. Chlorinated polyvinyl chloride was used as the initial chloropolymer, and nitrogen-containing carbon nanofibers (N-CNFs) were used as a nanoscale component. The structure of the resulting nanocomposites was examined by electron microscopy and the texture parameters were studied using low-temperature nitrogen adsorption–desorption. The introduction of N-CNFs into the carbon matrix and the activation of the resulting carbon–carbon nanocomposite in an atmosphere of CO_2 contributed to the formation of a micro- and mesoporous material with a specific surface area of ~1100 m²/g. It was shown that the resulting nanocomposites were characterized by high energy capacity and energy efficiency when tested as electrodes of electrochemical supercapacitors.

Keywords: carbon–carbon nanocomposites, polyvinyl chloride, carbon materials, carbon matrix, nitrogencontaining carbon nanofibers, porous materials, supercapacitor electrodes

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INTRODUCTION

One of the topical directions in the field of modern materials science is the controlled synthesis of functional carbon materials with desired properties, in particular, due to the incorporation¹ of nanodispersed modifiers into a carbon matrix. The advantage of nanocomposite type materials is the possibility of combining in them both the specific properties characteristic of nanosized particles and the useful properties of a matrix in which these particles are distributed. A large number of studies have been devoted to the preparation of nanocomposite carbon materials (CMs) [1-4], and these materials are used in medicine [5], agroindustry [6], and the environmental sphere [7, 8] as biosensors [9], electrodes [10], and components of electronic devices [11], and the scope of their use continues to expand. A separate area of research is the production of carbon-carbon nanocomposites (CCNCs), which contain carbon nanoparticles (carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphite oxide (GO), reduced graphite oxide (RGO), fullerenes, etc.) embedded in a carbon matrix. Despite all the variety of composite materials based on a carbon matrix and the lack of solubility and thermoplasticity of CMs, the direct incorporation of nanoparticles into this matrix is very difficult to perform. In this regard, nontraditional approaches to the preparation of nanocomposites, in particular, the

¹ The term *incorporation* includes the formation of composite structures that do not involve the formation of chemical bonds between the components.



Fig. 1. Schematic diagram of the formation of a carbon matrix from PVC.

introduction of nanomodifiers into various precursors of a carbon matrix with the further formation of carbon structures with nanoparticles distributed in them should be used. The use of this technique makes it possible to vary the characteristics of the final CMs within wide ranges. For example, the preliminary introduction of CNTs [12], CNFs [13], and GO [14] into the volume of biomasses (wood, lignin) before their carbonization made it possible to improve the mechanical and electrochemical characteristics of final materials, in contrast to materials obtained without additives. Zhang et al. [15] noted that the introduction of multilayer CNTs into a wood-based carbon matrix led not only to an improvement in strength characteristics but also to an increase in the specific surface area (compared to that of CMs without additives) and the formation of an ultramicroporous matrix; because of this, the resulting CCNCs showed high adsorption characteristics with respect to CO_2 and their applicability as electrodes of supercapacitors (SCs). The CCNCs were also synthesized by the carbonization of pulp and paper sludge modified with CNTs [16].

The resulting materials showed high performance when tested as cathode electrocatalysts for fuel cells. The CVD of carbon nanoparticles is a method for the synthesis of CCNCs. For example, Krasnikova et al. [17] obtained hierarchically structured porous CCNCs by CVD of CNFs from acetylene onto carbon microfibers with a nickel-containing catalyst. They noted that these materials can be used as separating membranes. CCNCs containing graphene nanoplates were obtained by the carbonization and graphitization of foamed petroleum pitch, into which the used nanoparticles were preliminarily introduced [18]. Compared to CMs that were not modified with graphene nanoplatelets, the CCNCs synthesized in this work showed improved electrochemical characteristics in tests as anode materials for lithium-ion batteries. CCNCs in the matrix of which graphene nanoplatelets or nanodiamond particles were distributed were obtained from coal tar pitch [19]. The introduction of these nanoparticles improved the electrical, mechanical, and thermal properties of the matrix.

In general, the introduction of a nanosized component can provide a material with desired properties and expand the scope of its use. Due to the combination of the unique properties of a carbon matrix (thermal and heat resistance, sorption properties, and a complex of specific electrophysical properties) and the introduced carbon nanoparticles (high conductivity, emission properties, and high specific surface area), the scientific development of the production of CCNCs in the field of synthesis of nanocomposite materials is of considerable current importance.

Previously, we proposed an approach to the preparation of CCNCs with nanoglobular carbon (NGC) and reduced graphite oxide (RGO) particles embedded in a carbon matrix [20, 21] based on the two-stage formation of an amorphous carbon matrix from commercially available carbon-chain chloropolymers (polyvinyl chloride (PVC), chlorinated PVC, and vinylidene chloride polymers and copolymers). At the first stage, dehydrochlorination of chloropolymers under the action of bases in organic media occurred with the formation of carbon-enriched polymers with a conjugation system (polyvinylenes); at the second stage, isolated polyvinylenes at temperatures to 400°C entered into interchain condensation with the formation of sp^2 -carbon structures [22]. Figure 1 shows a schematic diagram of the formation of a carbon matrix from chloropolymers using PVC as an example.

It should be noted that the dehydrochlorination of chloropolymers makes it possible to convert covalently bound chlorine into an ionic state, which excludes the formation of highly toxic organochlorine compounds upon the subsequent heat treatments necessary for the formation of the CM structure. Therefore, the proposed approach to the production of CMs makes it possible to solve the urgent problem of developing an environmentally significant technology for converting carbon-chain chloropolymers into required products under mild conditions. When using the proposed method, there is no release of hazardous organic substances into the atmosphere, which, for example, is observed in traditional processes for the disposal of polymer waste using high-temperature treatments (incineration).

The possibility of performing dehydrochlorination of chloropolymers in solutions made it possible to introduce modifying nanoadditives (RGO, NGC) into the carbon precursor at the stage of polyvinylene synthesis under mild conditions. Further carbonization and activation of the materials isolated after the dehydrochlorination of a carbon-chain chloropolymer with carbon additives led to the formation of porous CCNCs. We found that the incorporation of various nanodispersed modifiers into a carbon matrix makes it possible to vary the texture and properties of the resulting nanocomposites [20, 21]. In particular, we found that the modification of CMs with 1% RGO leads to the formation of a nanocomposite with a specific surface area of 1800 m²/g and a developed network of micro- and mesopores. The resulting CCNC exhibited high values of specific energy capacity (to 200 F/g in aqueous solutions of 1 M LiClO₄ and 6 M KOH with a potential sweep rate of 10 mV/s) when tested as an SC electrode.

In continuation of previous studies, in this work, we studied the possibility of introducing CNFs into a carbon matrix. We used the addition of mesoporous nitrogen-containing CNFs (N-CNFs) as a nanoscale modifier, in which multiple edges of graphene planes consisting of carbon and nitrogen atoms (the nitrogen content of N-CNFs was 3%) emerged on the outer surface [23, 24]. It is assumed that N-CNFs will serve as additional centers for the formation of a developed porous structure of the composite, while the nitrogen atoms of N-CNFs will facilitate the interaction of carbon fibers with chlorinated PVC. In our opinion, nanocomposites obtained with N-CNFs can be of practical interest as micro- and mesoporous adsorbents and electrodes for electrochemical SCs.

This work was devoted to the synthesis of CCNCs using an industrially available chloropolymer, chlorinated PVC (as a carbon matrix precursor), and a nanodispersed carbon modifier, N-CNFs, and to the study of physical and electrochemical characteristics of the resulting material.

EXPERIMENTAL

Chlorinated PVC from Khimprompostavka (Sterlitamak, Bashkortostan, Russia) with a Cl content of 61.5 wt % (GOST [State Standard] 10004-72) was used as a starting polymer material in this work.

The N-CNFs used in this study were obtained by decomposition of an ethylene–ammonia mixture on a Ni–Cu catalyst at 550°C [23]. The N/C ratio in the N-CNFs was 3 wt %, and nitrogen occurred in pyridine-like, pyrrole, and graphite-like electronic states with the predominance of pyridine-like nitrogen (>40%) [25].

The porous CM was prepared by a combination of chemical dehydrochlorination of chlorinated PVC and heat treatment of the resulting polyvinylene. The dehydrochlorination was carried out in a 1 wt % solution of the polymer in dimethyl sulfoxide (DMSO) in the presence of KOH (a polymer to alkali ratio was 1 : 2 by weight) at 20°C for 6 h with constant stirring.

An additive of 2–5 wt % N-CNFs on a chlorinated PVC basis was introduced into the reaction mixture

before the addition of alkali in the form of dispersion in DMSO. The dispersion of N-CNF particles in a solution of chlorinated PVC in DMSO was stabilized by ultrasonic treatment for 15–45 min with a UZD1-0.063/22 submersible ultrasonic disperser. The distribution of particles in the dispersion was determined using a Mikromed-1 optical microscope.

The dehydrochlorination product was precipitated in water, filtered off, and washed with water until the absence of Cl⁻ ions from the washing water.

The heat treatment of the isolated product (polyvinylene or a polyvinylene—N-CNF adduct) was carried out in a SNOL 7.2/1100 tube furnace in a flow of CO2 in two stages: carbonization (200 and 400°C, 2 h each) and activation (900°C, 1 h).

The morphology of the obtained materials was studied by transmission electron microscopy (TEM) using a TEM 2100 JEOL transmission electron microscope (accelerating voltage, 200 kV; lattice resolution, 0.14 nm) with an INKA 250 energy dispersive X-ray spectrometer (Oxford Instruments). The samples were also studied by energy dispersive spectroscopy (EDS) using a JSM-6460LV JEOL microscope equipped with an INCA x-Act X-ray microanalysis spectrometer (Oxford Instruments).

The textural characteristics of CMs were determined from an analysis of the nitrogen adsorption– desorption isotherms at 77 K obtained on a Micromeritics ASAP-2020M analyzer. The adsorption pore volume (V_{ads}) was determined from nitrogen adsorption at a relative pressure of 0.990. The micropore volume (V_{micro}) was evaluated using the α_s method. To obtain pore size distribution curves, the BJH method was used for an adsorption branch. The average pore diameter was calculated as a ratio of $4V_{ads}$ to S_{BET} .

Electrochemical studies were carried out in a universal asymmetric capacitor cell. The weight of a working electrode (5–9 mg) was chosen so that the capacity of an auxiliary electrode was greater than the capacity of the working electrode by a factor of ~50. This allowed us to consider the auxiliary electrode as conditionally nonpolarizable; in this case, a change in the cell voltage by 98% was determined by the polarization of the working (tested) electrode. The experimental cyclic current–voltage (CV) curves were presented in the form of capacitance–voltage dependences; for this purpose, the current was divided by the voltage sweep rate.

Since the capacitance of the auxiliary electrode was many times greater than the capacitance of the working electrode, the change in voltage under experimental conditions was determined by the potential of the working electrode relative to the stationary potential of the auxiliary one.

Four-layer electrodes based on high-capacity activated carbon fabric CH 900 from Kuraray (Japan)



Fig. 2. TEM images of (a) N-CNF and (b) a carbon matrix obtained without a nanocarbon additive.

were used as an auxiliary electrode. An aqueous 0.5 M solution of H_2SO_4 was used as an electrolyte.

RESULTS AND DISCUSSION

The synthesis of CCNCs included the following stages:

-Combination of chlorinated PVC solutions and a dispersion of N-CNFs in DMSO. The ratio between N-CNFs and chlorinated PVC was calculated based on the need to obtain final carbon nanocomposites with N-CNF concentrations of about 2 and 5%.

-Dehydrochlorination of chlorinated PVC (in the presence of an N-CNF additive) under the action of KOH at room temperature in order to synthesize polyvinylene (a carbon precursor).

-Carbonization of the isolated polyvinylene-N-CNF composition in an atmosphere of CO₂ at 200°C for 2 h and at 400°C for 2 h with the formation of sp^2 -carbon structures.

-Activation of the carbon structures obtained in step 3 at 900° C in order to develop a porous structure in the final CM.

Conditions for the preparation of stable N-CNF dispersions in the solvent used (DMSO) were determined in series of preliminary experiments. For this purpose, the ultrasonic treatment of DMSO with N-CNF agglomerates was carried out. The distribution of N-CNF particles in the solvent was assessed using an optical microscope. It was found that a relatively uniform distribution of N-CNF particles in the solvent volume occurred after 8 h of ultrasonic treatment of the test solution with the formation of a dispersion, which was stable for five days.

The formation of CCNCs was confirmed by TEM. Figure 2 shows TEM images of a carbon matrix synthesized under the same conditions as CCNCs but without the addition of a nanodispersed modifier (Fig. 2b) and N-CNFs used in this work (Fig. 2a). As can be seen in the image (Fig. 2a), the basal planes in carbon nanofibers were located at an angle of 45–90° relative to the fiber growth axis to form a fishbone or deck-of-cards packing. The CM sample (Fig. 2b) was a disordered amorphous carbon matrix without additional components in its volume.

The TEM images of CCNCs with introduced N-CNFs (Figs. 3a, 3b) exhibited CNFs with a diameter of 15–30 nm located in the bulk of a carbon matrix. The carbon matrix was characterized by a structure of disordered graphene layers typical of amorphous carbon. It is likely that voids located between nanofibers and matrix nanoparticles were responsible for the developed network of mesopores.

The results of the EDS analysis of CCNC samples with N-CNF additives confirmed the formation of a carbon material with a carbon content of at least 95% (Fig. 3c).

The porous structure parameters of the CCNCs were studied using the low-temperature adsorption– desorption of nitrogen. Figure 4 shows isotherms for the studied samples of activated carbon materials.

CMs without a modifier were characterized by a type I adsorption branch with a narrow hysteresis loop similar to type H4, which usually indicates the presence of predominant microporosity in the material. Nitrogen adsorption-desorption isotherms of N-CNF/CM compositions demonstrated an adsorption branch as a combination of type I and II isotherms according to the IUPAC nomenclature [26]. These isotherms are characterized by both a pronounced rise in the region of low P/P_0 associated with the filling of micropores and the presence of an H3type hysteresis loop in the region of higher relative pressures, which suggests the presence of a significant fraction of mesopores. The absence of saturation at $P/P_0 = 1$ indicates the presence of macropores that are



Fig. 3. (a, b) TEM images of CCNC in which N-CNFs are distributed in the bulk of an amorphous carbon matrix and (c) a fragment of the EDS spectrum of this sample.



Fig. 4. Isotherms of the low-temperature adsorption–desorption of nitrogen and pore size distribution curves of (1) CM without additives and the CCNCs (2) 2% N-CNF/CM and (3) 5% N-CNF/CM.

not completely filled with condensate in the porous space.

Based on an analysis of the experimental isotherms, the texture parameters of porous CCNCs and CMs without additives were calculated (Table 1). As can be seen in Table 1, a CM in the absence of a modifying additive was almost a microporous material, and the fraction of micropores was 86%. The introduction of 2% N-CNFs into a carbon matrix contributed to a slight increase in the specific surface area with a pronounced development of mesoporosity

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Material	S _{BET} , m²/g	$V_{\rm micro},$ cm ³ /g	$V_{\rm meso},$ cm ³ /g
5% N-CNF/CM	1097	0.33	0.71
2% N-CNF/CM	772	0.21	0.46
СМ	651	0.25	0.04
N-CNF	338	0.01	0.73

Table 1. Textural parameters of porous CCNCs, N-CNFs,and the CM without modifiers

compared to CMs without N-CNFs; the mesopore volume increased from 0.04 to 0.46 cm³/g to reach 70% of the total pore volume. The introduction of 5% N-CNFs led to even more significant changes in the porous structure parameters and the specific surface area. Thus, the specific surface area and the volume of micropores increased by a factor of 1.5 from 651 to 1097 m²/g, and the volume of mesopores became 0.71 cm³/g; in this case, a ratio between the contributions of micropores and mesopores remained the same as that upon the introduction of 2% N-CNFs.

Figure 4a shows pore size distribution curves (PSDCs) obtained using the BJH method. Upon the introduction of 2% N-CNFs, the PSDC of the composite had a pore size distribution in a range of 3–100 nm with a pronounced contribution of mesopores to 30 nm and a PSDC maximum at 15 nm. The introduction of 5% N-CNFs led to a broader PSDC to 200 nm with an increase in the contribution of large mesopores (30– 50 nm) and a fraction of macropores, and the main distribution maximum shifted to 50 nm.

From an analysis of the experimental data, we concluded that the introduction of nanofibers significantly contributed to the formation of mesoporosity in



Fig. 5. Cyclic capacitance–voltage curves of 5% N-CNF/CM at a sweep rate of 10 mV/s: (1) before the potential of reduction and (2) at more negative potentials.

composite materials, probably, due to the formation of an additional porous space between the embedded fibers and the carbon matrix. The addition of 5% nanofibers led to a wider distribution of pores in CMs with the highest specific adsorption pore volume due to the formation of a significant fraction of large mesopores. Thus, the introduction of 2-5% N-CNFs into an amorphous carbon matrix made it possible to obtain micro- and mesoporous CMs with a developed porous structure and a contribution of mesopores to the total pore volume up to 70%. A similar trend was observed when RGO was introduced into a PVCbased carbon matrix: the specific surface area and the fraction of mesopores increased in comparison with those in the material obtained without the addition of carbon nanoparticles [21].

In view of the fact that a micro- and mesoporous carbon composite with a specific surface area of more than 1000 m²/g (which meets the requirements imposed on the characteristics of SC electrodes) was obtained upon the introduction of 5% N-CNFs, this sample was studied as an electrode of an electrochemical SC.

The resulting CCNCs showed a relatively rapid hydrophilization in the course of electrochemical tests: an increase in the capacitance a day after contact with the electrolyte did not exceed 5%. The average capacitance at potential sweep rates from 5 to 20 mV/s was ~100 F/g. This capacitance is comparable with typical values for micro- and mesoporous materials with a specific surface area of ~1000 m²/g [27].

The surface of the material contained oxidized structures (probably containing oxygen), the irreversible reduction of which began at potentials lower than -450 mV (Fig. 5). After five or six cycles at a potential sweep rate of 10 mV/s, cyclic capacitance–voltage curves (CVCs) acquired a stable nearly rectangular shape, which is characteristic of charging a double electric layer (EDL) [28, 29].

The nearly rectangular shape of the cyclic CVCs allowed us to conclude that the energy efficiency (a ratio of the discharge energy to the charge energy) of this material can be higher than the efficiency of classical microporous coals, which are characterized by specific sorption tails at the edges of the EDL charging interval during testing in acidic media [30]. An increase in cathodic polarization did not lead to an increase in anode capacity, which also distinguishes this material from classical microporous activated carbons [31].

The CVC curve exhibited a number of explicit and hidden maximums, which were most likely due to the presence of surface functional groups of various natures, including nitrogen centers of N-CNFs [28, 29, 32]. Microporous coals always exhibited a significant increase in the anode (discharge) capacity with an increase in the range of charging to the region of



Fig. 6. Cyclic capacitance–voltage curves at a sweep rate of 10 mV/s: (1) steady-state curve before oxidation and (2) curve after oxidation.

negative potentials due to the specific sorption of ions in micropores.

One of the features of this material is a significant increase in capacity from 100 to 200 F/g in the course of electrochemical oxidation (Fig. 6), probably, due to redox reactions of surface groups. This fact allowed us to consider a significant contribution of surface structures close to the prismatic planes of a graphite crystal in terms of reactivity.

According to electrochemical data, the CCNC obtained can be recommended for SCs used to smooth out peak loads in electrical networks [33, 34]. This is due to relatively high energy efficiency. As found previously [31, 35], the energy efficiency of a double-layer capacitor characterized by a rectangular shape of cyclic current–voltage and capacitance–voltage curves approaches 100% due to the absence of electrochemical polarization, which is observed in batteries. After oxidation, which leads to the hydrophilization of carbon materials and, consequently, to an increase in their capacity in aqueous electrolytes, this material can be recommended for traction (energy) electrochemical SCs [36, 37].

CONCLUSIONS

We obtained compositions of carbon-enriched polyvinylene (a reactive precursor of carbon, the product of chloropolymer dehydrochlorination) modified with N-CNF particles. Thermal treatment of the resulting compositions in an atmosphere of CO_2 for the purpose of their carbonization and activation led to the formation of porous CCNCs with nanofibers embedded in the bulk of the carbon matrix, which was confirmed by electron microscopy.

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We found that the use of N-CNFs as a modifying additive makes it possible to significantly change the textural properties of the new material compared to those of microporous carbon formed in the absence of a nanosized modifier. The introduction of N-CNFs into the carbon matrix contributed to the formation of micro- and mesopores in the material with a significant predominance (up to 70%) of mesopores.

According to the data of electrochemical studies, the combination of two types of carbon structures in the developed material with the specific surface area $S_{\text{BET}} > 1000 \text{ m}^2/\text{g}$ and an optimal ratio between microand mesopores for the accumulation of electric charge provides sufficiently high values of the electrical capacitance (about 200 F/g) and energy efficiency (approaching 100%). SCs with these electrodes can be recommended for smoothing out peak loads in electrical networks.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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