08

Nanostructures based on carbon nanotubes and manganese oxide to enhance the electrochemical characteristics of carbon black

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A composite based on multi-walled carbon nanotubes and manganese oxide with the addition of silver was obtained by liquid chemical deposition. It has been established that under this synthesis mode, a layer consisting of randomly oriented K_xMnO_2 nanocrystallites with a high interplanar distance (up to 6.5 Å) is formed on the surface of the carbon nanotubes. It is shown that the resulting composite can be promising as an active component for increasing the capacitance and rate characteristics of commercial grades of carbon black when used in supercapacitors.

Keywords: supercapacitor, specific capacitances, redox reactions, rate capability.

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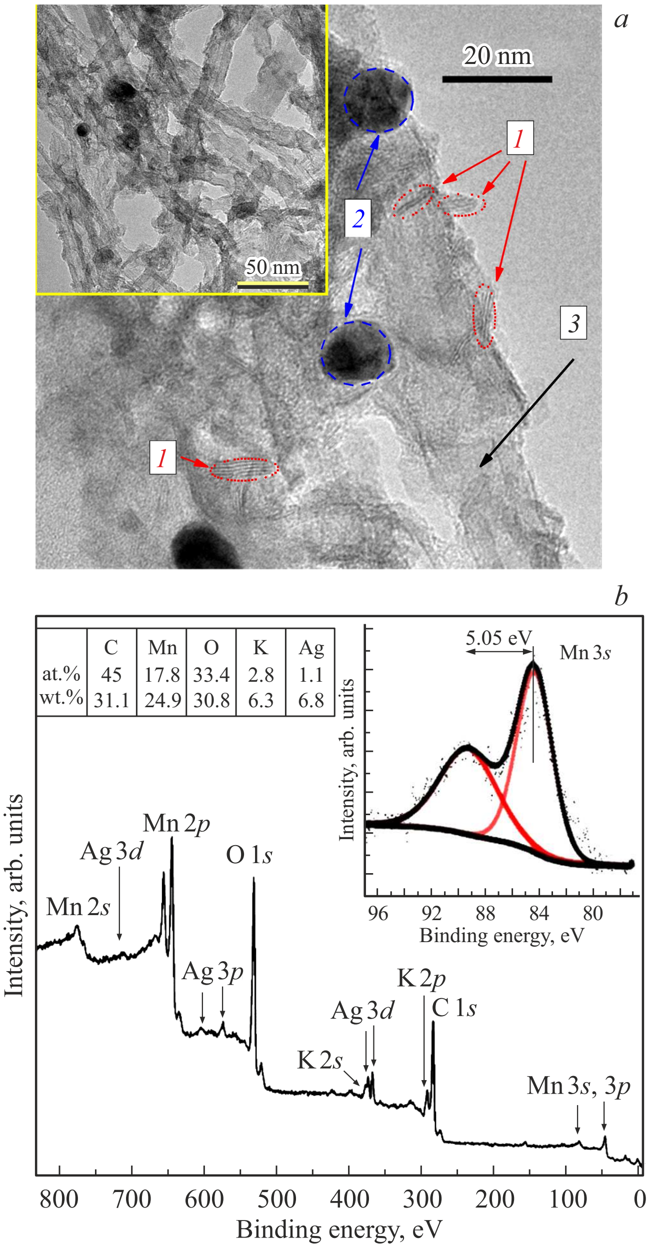
Supercapacitors (SCs) — are energy storage devices with high specific values of power density. SCs are used in those cases when the high speed of charge storage and return, long-term operation in the charge/discharge mode, and packet energy transfer [1] are necessary. Energy storage in SCs is implemented due to the formation of a electric double layer (EDL) at the boundary of the electrode material surface contact with electrolyte, or at the expense of the behavior of redox reaction. The first mechanism of charge storage is specific for carbon electrode materials demonstrating high cyclic stability and charge/discharge rate. The second mechanism of charge storage (pseudocapacity) is implemented with participation of the active materials — oxides of transition metals, which under interaction with the electrolyte ions reversibly change their oxidation degree. Metal oxides may store a large quantity of charge per unit of mass compared to carbon materials. However, they low power characteristics due to high electrical resistance, as well as insufficient cyclic stability [1,2]. Development of composite materials, which harmonically combine both energy storage mechanisms, open the possibility to create the devices with improved energy-capacitance characteristics. This paper studied the structure and electrochemical characteristics of the composite produced on the basis of multi-walled carbon nanotubes (MWCNTs) and manganese oxide doped with potassium and silver ($Ag@K_xMnO_2$/MWCNT). Besides, the electrochemical characteristics of the combined electrode materials were studied on the basis of the produced composite and commercial carbon black (CB).

The synthesis of the composite was carried out using MWCNTs with diameter of $\sim 5-7$ nm and the value of the specific surface area $\sim 360\,m^2/g$ (MWCNT-1, made by Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Russia), which after the prior treatment in 30% HNO_3 for 30 min were soaked in aqueous solution $KMnO_4$ with addition of $AgNO_3$ at 60°C under constant stirring with speed of $25\,s^{-1}$ for 6 h. Mass ratio of $MWCNT:KMnO_4:AgNO_3:H_2O$ was $1:10:0.2:1000$. The produced composite after washing and drying was mixed with the commercial CB at mass ratio of 1 : 1. CB grades „Printex XE-2B“ (ORION, Germany) and „OMCARB CH1000“ (made by LLC „Omsktekhuglerod“, Russia) were used with the specific surface area values of more than $1000\,m^2/g$ were used. Electrodes were made using a polymer binder (10 wt%) according to the method described in [3]. Electrochemical characteristics of the electrodes were analyzed according to a three-electrode scheme with application of cyclic voltammetry (CV), and also the method of galvanostatic charge-discharge (GCD) in 1 M Na_2SO_4 as electrolyte. The legend of the electrodes with different composition are presented in Table 1.

Analysis of the composite structure using the method of transmission electron microscopy (TEM) showed that MWCNTs in the composite are coated with layers of the substance, crystallites of which (are indicated by figure *1* in Figure 1, *a*), according to the fast Fourier transform data, have the values of interplanar spacing 0.63–0.65 nm, which, according to the literature data, corresponds to

Table 1. Composition and legend of electrodes

Composition of electrode	Legend
MWCNT-1	CNT
TC Printex XE-2B	PR
TC OMCARB CH1000	CH
Composite Ag@K_xMnO_2/MWCNT	K100
Composite Ag@K_xMnO_2/MWCNT (50 wt%) + TC OMCARB CH1000 (50 wt%)	K50 + CH50
Composite Ag@K_xMnO_2/MWCNT (50 wt%) + TC Printex XE 2B (50 wt%)	K50 + PR50



	C	Mn	O	K	Ag
at.%	45	17.8	33.4	2.8	1.1
wt.%	31.1	24.9	30.8	6.3	6.8

Figure 1. *a* — TEM images of composite Ag K_xMnO_2/MWCNT (*1* — crystallites K_xMnO_2, *2* — crystallites Ag_2O, *3* — MWCNT); *b* — results of XPS analysis of composite Ag@K_xMnO_2/MWCNT (main figure — survey spectrum, inserts show spectrum Mn3*s* and results of the quantitative analysis).

compound K_xMnO_2 (for MnO_2 the interplanar spacing is 0.21–0.30 nm) [4]. Denser nanoparticles are also observed (average size ~ 10 nm), the interplanar spacing in which is 0.24–0.27 nm, which corresponds to silver oxide Ag_2O (Figure 1, *a*).

The method of X-ray photoelectron spectroscopy (XPS) showed that in the composite the ratio of atomic concentrations of oxygen and manganese practically corresponds to compound MnO_2 with a minor deficit of oxygen in Figure 1, *b*). The energy distance between maxima of Mn3s doublet is 5.05 eV (see insert with spectrum in Figure 1, *b*). The estimate of the manganese oxidation degree with account of the formula presented in [5], makes it possible to say that its value is 3.26. This confirms the availability of compounds KxMnO$_2$ in the composite. Atomic concentration of silver within the composition is low. With account of silver particle distribution density in the composite on TEM images one can assume that the substantial part of silver is found specifically in individual nanoparticles. The maximum position in XPS-spectrum of Ag3$d_{5/2}$ (not presented in the figures) corresponds to oxide Ag_2O (368.0 eV), which is matched to the results of the TEM image analysis. One can also see from the results of the qualitative XPS analysis that the bulk load of MWCNT composite is around 30% (Figure 1, *b*).

The specific capacitances of electrodes was determined by examining galvanostatic discharge curves as a product of the discharge current density (A/g) and the discharge time (s) referred to the potential range (V). The specific capacitances value was determined both in „standard" charge-discharge mode (C_1, F/g) and when charged in the mode of „direct current/direct voltage" (C_2, F/g), when the electrode was additionally charged at maximum voltage for 300 s prior to discharge (Figure 2, *a*).

One can see that the discharge time and specific capacitances after the additional charge increase for all electrodes, at the same time, as the current density increases, the difference in values C_1 and C_2 noticeably grows (Figure 2, *a*, Table 2). Efficiency of additional charge in the mode of „direct current/direct voltage" ($E = C_2/C_1$, Table 3) apparently depends directly on the charge storage mechanism: as the contribution of redox reactions limited by time with electrolyte ion diffusion into the electrode volume, the value E increases.

For K100 electrode the value E is next higher order compared to the other electrodes (Table 3). Electrodes

Table 2. Specific discharge capacity of electrodes with different composition when charged in mode of „direct current“ (C_1, F/g) and in mode of „direct current/direct voltage„ (C_2, F/g)

Current density, A/g	PR		CH		K100		K50 + CH50		K50 + PR50	
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
0.1	52.5	58.8	69.3	76.0	118.0	125.5	89.4	94.5	78.3	89.3
0.2	47.3	57.0	65.5	76.0	102.3	116.0	86.5	93.0	72.5	84.8
0.3	43.4	54.9	62.0	75.1	88.5	107.9	81.4	90.3	67.2	80.6
0.4	39.0	52.3	59.3	73.8	77.5	101.0	76.3	87.8	63.3	77.0
0.5	36.3	49.8	57.5	72.0	67.0	94.8	72.8	85.5	59.5	73.8
1.0	24.5	37.5	44.0	62.3	27.0	70.5	52.5	72.0	41.8	60.8
2.0	6.5	20.6	20.8	46.3	0.5	35.3	25.3	52.0	19.0	42.5

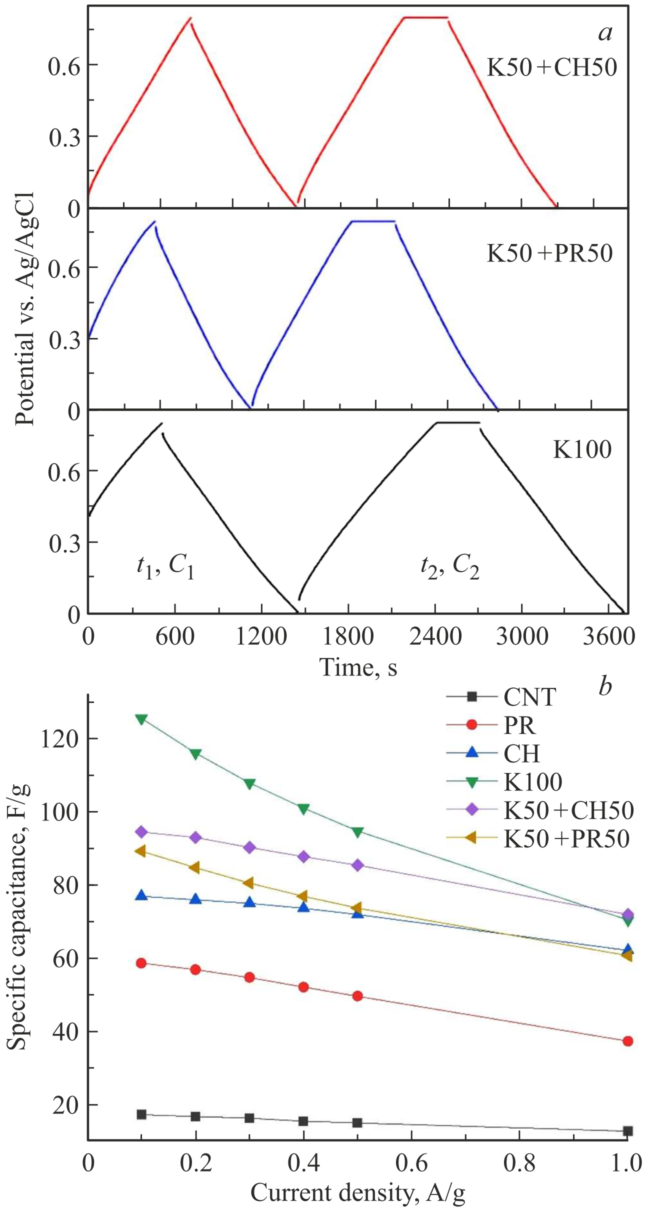


Figure 2. *a* — charge-discharge curves of electrodes measured at current density 0.1 A/g; *b* — dependence of specific discharge capacity C_2 on discharge current density for electrodes of different composition.

Table 3. Characteristics $R = (C_2(2.0\,\mathrm{A/g})/C_2(0.1\,\mathrm{A/g}) \cdot 100\%$ and $E = C_2(2.0\,\mathrm{A/g})/C_1(2.0\,\mathrm{A/g})$ for electrodes of different composition

Electrode	R, %	E
PR	35.0	3.17
CH	60.9	2.23
K100	28.1	70.60
K50 + CH50	55.0	2.06
K50 + PR50	47.6	2.24

based on CB (PR and CH) store the charge in EDL, therefore, when their values E (Table 3) are compared, one can conclude on the higher availability of the CH electrode surface for the electrolyte ions, compared to the PR electrode. Rate capability of electrodes (R, %) was assessed by the ratio of the specific capacitances C_2 values at current densities 2.0 and 0.1 A/g (Table 3). CH and PR electrodes maintain $\sim 60\%$ and 35% values of specific capacitances as discharge current density increases 20 times. At the same time the results of measurement using a four-probe method demonstrated that the value of specific conductivity for the PR electrode is even slightly higher compared to CH electrode (0.38 ± 0.02 and 0.1 ± 0.01 Sm/cm, accordingly). This result shows that the higher specific capacitances and rate capability of the electrode based on OMCARB CH1000 compared to electrode based on Printex XE-2B were due to, first of all, the structural and morphological features (dimensions of CB globules and pores, pore size distribution).

K100 electrode at current density 0.1 A/g has the value of specific capacitances $C_2 = 125.5$ F/g (Table 3), which decreases practically by 72% as the current density increases 20 times (R in Table 3) This, first of all, is related to insufficient electroconductivity of MWCNTs coated with a layer K_xMnO_2. Electrodes on the basis of CB and composite combination (K50 + CH50 and K50 + PR50) at current density 0.1 A/g have higher values of specific capacitances compared to electrodes on the basis of CB only (CH and PR). The increase is around 24% and 52% for the cases of OMCARB CH1000 and Printex XE-2B, accordingly

(Figure 2, *b*, Table 2). Combined electrodes (K50 + CH50 and K50 + PR50) are noticeably inferior in the specific capacitances value to K100 electrode at low current density, however, already at current density 1.0 A/g the values of specific capacities C_2 for them are comparable to K100 electrode. With the further double increase of the discharge current density up to 2.0 A/g the specific capacitances of the latter is inferior to electrodes K50 + CH50 and K50 + PR50. Maximum specific capacitances C_2 at high current density is observed for electrode K50 + CH50 (52 F/g).

The value of specific capacitances C_2 of combined electrodes at current density 2.0 A/g is 120 and 200% orelative to capacity C_2 of the electrodes on the basis of only CB, grades OMCARB CH1000 (CH electrode) and Printex XE-2B (PR electrode), accordingly (Figure 2, *b*, Table 2). For K50 + PR50 combination there is also a noticeable growth in the value of rate capability (*R*, Table 3) not only compared to the K100 electrode, but also relative to PR electrode. This is presumably related to formation of additional channels for charge transport, and increase in the area of the electrochemically active surface available for electrolyte ions, as the composite is distributed in the CB porous matrix.

The results obtained in the paper show that the formed composite Ag@K_xMnO$_2$/CNT is an effective active additive, providing for considerable increase of electrochemical characteristics of CB in a wide range of current loads. High specific capacitances and rate capability of the electrodes on the basis of the combination of the composite and CB is provided by the unification of material properties with various charge storage mechanisms.

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Conflict of interest

The authors declare that they have no conflict of interest.

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