Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2014, **24**, 304–305

Mendeleev Communications

# Adsorption-induced functionalization of carbon nanowalls

**Liana N. Sviridova,*[a] Victor A. Krivchenko,[b] Kirill V. Mironovich,[b]
Pavel V. Voronin,[b] Aleksandr G. Krivenko[c] and Elena V. Stenina[a]**

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: + 7 495 939 0171; e-mail: slianan@mail.ru*
[b] *D. V. Skobeltsyn Institute of Nuclear Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*

DOI: 10.1016/j.mencom.2014.09.019

**The adsorption of camphor, sodium cryptate and 1-hydroxyadamantane on electrodes formed by vertically oriented carbon nanowalls (graphene-like material) leads to a substantial increase in a double-layer capacitance.**

The carbon nanowall (CNW) films exhibit unique properties, namely, a high electronic conductivity and a large specific surface area accessible for electrolyte solutions.[1] The area of potential applications of CNW films can be extended by their covalent or non-covalent functionalization.[2] However, the electrochemical and adsorption properties of this material are insufficiently clear. The effect of anodic pretreatment of the CNWs on their capacitance has been studied previously.[3] By analogy with highly oriented pyrolytic graphite,[4] Krivchenko *et al*.[3] assumed that the electrooxidation of CNW also leads to the appearance of functional quinone-hydroquinone surface groups (covalent functionalization) accompanied by a considerable increase in the electrochemical capacitance. This was explained by an increase in the CNW surface area due to a loosening of this material during its electrochemical functionalization.

The adsorption of small organic molecules (acetone, acetonitrile, dichloromethane, ethanol, ethyl acetate, hexane and toluene) on graphene has been reported.[5] It was shown experimentally that the adsorption enthalpy ($\Delta H_{\mathrm{ads}}$) increases in the order $CH_2Cl_2$ < EtOH < acetonitrile < acetone < EtOAc < < hexane < toluene and depends on surface coverage. Initially, adsorption occurs on graphene with high surface energy (edge regions). After the edge regions are filled, the adsorption occurs on graphene planes. This follows from a constant value of $\Delta H_{\mathrm{ads}}$ at higher coverage. Adsorption enthalpies are mainly determined by the energy of adsorbate interaction with the surface, and adsorbed molecules do not change the electronic structure of graphene.

The adsorption of camphor on electrodes formed by single-walled carbon nanotubes (SWCNT) and columnar structures of multi-walled carbon nanotubes was studied.[6] Camphor is a surfactant which can form condensed adsorption layers (CALs) on electrodes with smooth surfaces (mercury, bismuth, zinc and tin). These layers are characterized by a high attraction constant ($a$ = 5–6), which points to the much more intense intermolecular interaction in the adsorption layer as compared with simpler organic compounds. The adsorption of CAL of this type on smooth electrodes is characterized by very low differential capacitance ($C$) of electric double layer (~3.6 μF cm$^{-2}$), corresponding to virtually maximum electrode coverage with adsorbate. At the same time, it was shown[6] that, in the presence of camphor, the differential capacitance increases (by a factor of 3–5) as compared with that of adsorbate-free solutions throughout the test potential range. This fact was explained by an increase in the electrode surface area, sufficiently large to override the capacitance decrease upon surfactant adsorption. For electrodes based on nanostructured carbon, such surface loosening and the concomitant increase in the electrolyte-accessible surface area results from the Rehbinder effect. From the thermodynamic standpoint, the latter is a decrease in the free surface energy of a solid under the action of the environment.[7] The molecular nature of this effect consists in the easier rupture and reconstruction of intermolecular bonds in a solid in the presence of surfactant species.[8]

Since the CNWs are promising material for supercapacitors,[1] the increase in their capacitance is a topical issue.

This study deals with electrodes modified with the films of CNWs, which represent a dense array of graphene-like sheets vertically oriented with respect to a conducting substrate (glassy carbon, nickel). Typical SEM images of the CNW films are presented in Figure 1. The height and linear size of the CNWs are 1 and 0.5–1 μm, respectively.

We used the following surfactants: camphor, 1-hydroxyadamantane (AdOH) and cryptand 2.2.2 (CR). The adsorption behavior of the surfactants was studied earlier in detail and characterized quantitatively for a wide range of electrodes;[6,9–13] this makes it possible to carry out a comparative analysis of the results.[†]

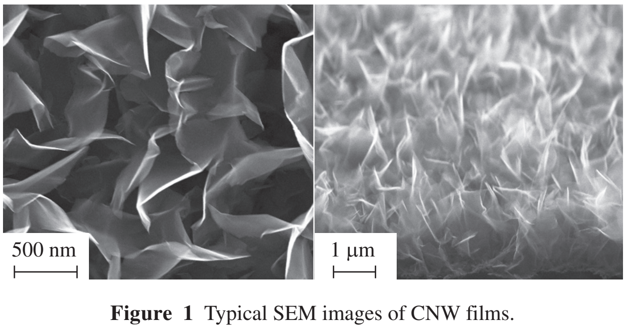

**Figure 1** Typical SEM images of CNW films.

---

[†] The experiments were carried out in a three-electrode cell by cyclic voltammetry and impedance spectroscopy on SNW electrodes in aqueous solutions of $Na_2SO_4$ (supporting electrolyte) in the absence and in the presence of surfactants. Using an AUTOLAB potentiostat–galvanostat, cyclic voltammograms (CVAs) and differential capacitance ($C$)–potential ($E$) relationships were measured at the ac frequency $f$ = 370 Hz in a potential range from –0.5 to +0.5 V.

Sodium sulfate was purified by double crystallization and annealed at 500 °C. Solutions were prepared with water purified in a Milli-Q system and deaerated with high-purity argon. Potentials were measured with respect to a saturated calomel electrode.

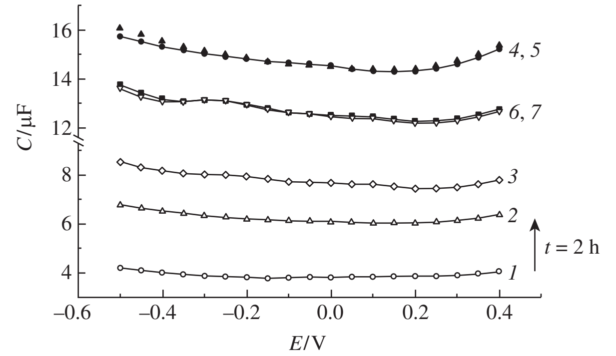

**Figure 2** *C*–*E* relationships for the CNW electrode in 0.1 M $Na_2SO_4$ solution (*1*)–(*3*) in the absence and (*4*)–(*7*) in the presence of camphor ($8\times10^{-3}$ mol $dm^{-3}$). Curves *4* and *6* correspond to 15 min of contact of CNW electrode with solution containing camphor, curves *5* and *7* – 30 min.

Prior to measurements, all samples were polarized at a potential scan rate of 50 mV $s^{-1}$ (10–15 cycles) in a supporting electrolyte solution (0.1 M $Na_2SO_4$) in order to determine the electrochemical window of potentials. The gravimetric capacity obtained from cyclic voltammograms (CVAs) in the supporting electrolyte was 20 F $g^{-1}$.

Figure 2 shows the dependence of *C* on *E* for a glassy-carbon-supported CNW electrode in a pure 0.1 M $Na_2SO_4$ solution (curves *1*–*3*) and in the presence of $8\times10^{-3}$ mol $dm^{-3}$ camphor (curves *4*–*7*). Almost constant values of *C* values were reached in 2 h (curves *1*, *2*). Such a behavior may be due to the gradual wetting of the CNW film, since as-grown films exhibit hydrophobic properties. In the solution with camphor, a jump-like increase in the capacitance (up to 2.5 times) with its further insignificant variation in time was observed, as compared with the maximum *C* in the supporting electrolyte (curves *4*, *5*). The increase in the measured capacitance can be associated only with an increase in the double layer electrode capacitance since CVAs demonstrate no faradaic currents in the test potential region; *i.e.*, the faradaic capacitance contribution was virtually absent. Similar results were obtained for the CNWs grown on a Ni support.

Note that the above effect is reversible. After the electrode was exposed in water for several hours, the capacitance in 0.1 M $Na_2SO_4$ solution reacquired its low values close to those reached in the first experiments before surfactant addition (curve *3*), while re-addition of camphor resulted in a jump-like increase in the capacitance (curves *6*, *7*).

Since the formation of CAL on smooth electrodes usually leads to a decrease in capacitance (3-4 times), the experimentally observed growth of the CNW electrode capacitance in the presence of camphor can be explained (by analogy with SWCNT electrodes) by a significant increase in the electrode effective surface area accessible for the electrolyte. Figure 1 shows that the morphology of as-grown CNW films is reasonably complex, and it can contain regions inaccessible to electrolyte due to van der Waals interaction between discrete CNWs. However, CAL absorption on the CNW surface leads to expansion due to the Rehbinder effect. Consequently, we actually observed an increase in the material surface area accessible to the electrolyte leading to a growth of the double layer capacitance. A similar effect of camphor on effective electrode surface area has been observed for samples composed of the SWCNT bundle.[6]

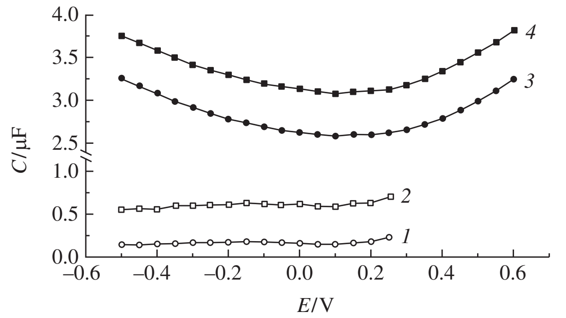

**Figure 3** *C*–*E* relationships for the CNW electrodes in 0.1 M $Na_2SO_4$ solution (*1*, *2*) in the absence and (*3*, *4*) in the presence of CR ($8\times10^{-3}$ mol $dm^{-3}$). Curves *1* and *3* correspond to 15 min of contact of CNW electrode with solutions (*1*) in the absence and (*3*) in the presence of CR, curves *2* and *4* – 60 min.

Qualitatively analogous effects were revealed in $Na_2SO_4$ solutions with the additions of CR (Figure 3) and AdOH. In the presence of these surfactants, the extension of the region of electrode ideal polarizability, the insignificant slow increase in capacitance with time in the supporting electrolyte solution and the jump-like increase in capacitance in solutions containing surfactants (in the presence of CR, by a factor of about 5) were observed. In AdOH-containing solutions, the surfactant-induced increase in capacitance was less pronounced. We associated this with the lower concentration of AdOH ($8\times10^{-4}$ mol $dm^{-3}$) because of its limited solubility.

The experimentally observed increase in the capacitance of the CNW electrodes at surfactant adsorption (despite the decrease in specific capacitance) may be explained by a predominance of effect of increase in the CNWs/electrolyte interface owing to the partial loosening of the CNW film. According to our estimation, the CNW effective surface area grows by a factor of 8–15 due to adsorption.

Thus, we observed the adsorption-induced functionalization of the CNW electrodes leading to a significant increase in the CNW effective surface area and, consequently, an increase in the double layer capacitance.

This work was supported by the Russian Foundation for Basic Research (grant nos. 13-03-00548 and MK-2773.2014.2).

## References

1 M. Cai, R. A. Outlaw, S. M. Butler and J. R. Miller, *Carbon*, 2012, **50**, 5481.
2 V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156.
3 V. A. Krivchenko, Yu. M. Maksimov, B. I. Podlovchenko, A. T. Rakhimov, N. V. Suetin and M. A. Timofeev, *Mendeleev Commun.*, 2011, **21**, 264.
4 H.-S. Choo, T. Kinumoto, M. Nose, K. Miyazaki, T. Abe and Z. Ogumi, *J. Power Sources*, 2008, **185**, 740.
5 P. Lazar, F. Karlicky, P. Jurecka, M. Kocman, E. Otyepkova, K. Safarova and M. Otyepka, *J. Am. Chem. Soc.*, 2013, **135**, 6372.
6 A. G. Krivenko, N. S. Komarova, E. V. Stenina and L. N. Sviridova, *Mendeleev Commun.*, 2009, **19**, 317.
7 P. A. Rehbinder, *Izbrannye trudy (Selected Works)*, Nauka, Moscow, 1978, p. 368 (in Russian).
8 B. Gao, A. Kleinhamme, X. P. Tang, C. Bower, Y. Wu and O. Zhou, *Chem. Phys. Lett.*, 1999, **307**, 153.
9 B. B. Damaskin and E. V. Stenina, *J. Electroanal. Chem.*, 1993, **349**, 31.
10 E. V. Stenina and L. N. Sviridova, *Russ. J. Electrochem.*, 2005, **41**, 414 (*Elektrokhimiya*, 2005, **41**, 475).
11 E. V. Stenina and L. N. Sviridova, *Elektrokhimiya*, 1994, **30**, 340 (in Russian).
12 V. V. Batrakov, B. B. Damaskin and Yu. P. Ipatov, *Elektrokhimiya*, 1974, **10**, 144 (in Russian).
13 E. V. Stenina and L. N. Sviridova, *Mendeleev Commun.*, 2013, **23**, 282.
14 V. Krivchenko, P. Shevnin, A. Pilevsky, A. Egorov, N. Suetin, V. Sen, S. Evlashin and A. Rakhimov, *J. Mater. Chem.*, 2012, **22**, 16458.
15 A. G. Krivenko, N. S. Komarova and N. P. Piven, *Electrochem. Commun.*, 2007, **9**, 2364.

*Received: 4th February 2014; Com. 14/4301*

---

The CNW films were synthesized by plasma-enhanced chemical vapor deposition without a catalyst on glassy carbon and nickel substrates. Experimental details were described elsewhere.[14] The method of electrode preparation was similar to the reported[15] for SWCNT electrodes.