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Electrochemistry of nanostructured carbon

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Abstract. The results of studies on the electrochemical behaviour of electrodes made of nanostructured carbon (single- and multi-walled nanotubes, nanopaper, nanofibres) and of conventional electrodes modified with these nanoobjects are analysed. Specific features of electrode reactions on modified electrodes that are not associated with their high specific surface areas are revealed. The bibliography includes 159 references.

I. Introduction

At the end of the past century, many scientists started declaring prospects of using nanotube carbon materials in electrochemistry. The following application fields were assumed to be the most attractive: in supercapacitors,[1–4] in lithium batteries,[5–7] for hydrogen storage[8–10] and as electrochemical sensors.[11–13] These materials were also proposed to be used as electrodes with electrocatalytic properties.[14,15] Hence, investigations of the electrochemical behaviour of nanotube electrodes were included into the plans of many research centres. After *ca.* 10 years, we can summarise the intermediate results.

This review focuses attention on the peculiarities of reactions that proceed on electrodes containing nanostructured † carbon of different morphology, but are not related to their high specific surface areas. In particular, these peculiarities may include the overpotential drop, the changes in mechanisms of electroreduction (ER) or electrooxidation (EO) of organic and inorganic depolarisers, electrocatalysis and the enhanced sensitivity of electrochemical detection of trace impurities. It seems obvious that these effects not observed for conventional carbon materials can be caused by either the presence of areas with high curvature (due to linear or point defects, open ends of nanotubes, *etc.*) on the surface of nanostructured electrodes or functionalisation of carbon nanomaterials.

The side surface of nanotubes, especially, single-walled ones also has high curvature; however, the majority of authors believe that the electrochemical properties of a defect-free side surface do not differ from the corresponding properties of common carbon materials. Particularly, the substantial decrease in the silver reduction overpotential on the defective surface of nanotubes as compared with the defect-free surface was used to detect and identify defects.[16] The present review briefly analyses the effect of the nanotube surface structure on the physical parameters that may affect its electrochemical characteristics. In the absence of such an effect, the electrochemistry of nanostructured carbon would merely be reduced to a branch of electrochemistry of carbon materials.

II. Structure of nanotubes and the emission currents

To date, a wide diversity of carbon nanotubes were synthesised. The most popular types are single-walled carbon nanotubes (SWNT), which consist of a single planar atomic plane of graphite (graphene) rolled up into a seamless cylindrical tube (Fig. 1 *a*,*b*), and multi-walled nanotubes (MWNT), which include from 2 to 50 coaxially embedded graphene cylinders or cones spaced by 0.34 nm (see Refs 18, 19). The ends of closed nanotubes have conical or hemispherical caps, which, in contrast to side surfaces, contain not only six- but also five-membered carbon rings.

It should be noted that, in addition to hollow cylindrical nanotubes, conical, helical, horn-shaped, bamboo-like (consisting of separate elongated closed sections) tubes, tubes assembled of alternating cones, and also L-, T- and Y-shaped structures can be produced depending on conditions of synthesis. Moreover, recently, the so-called 'nanopods', *i.e.*, nanotubes stuffed with C_{70} or C_{60} fullerenes were synthesised.

† In the present review, under nanostructured carbon, the different types of carbon nanotubes and nanofibres used for fabrication of electrodes are meant.

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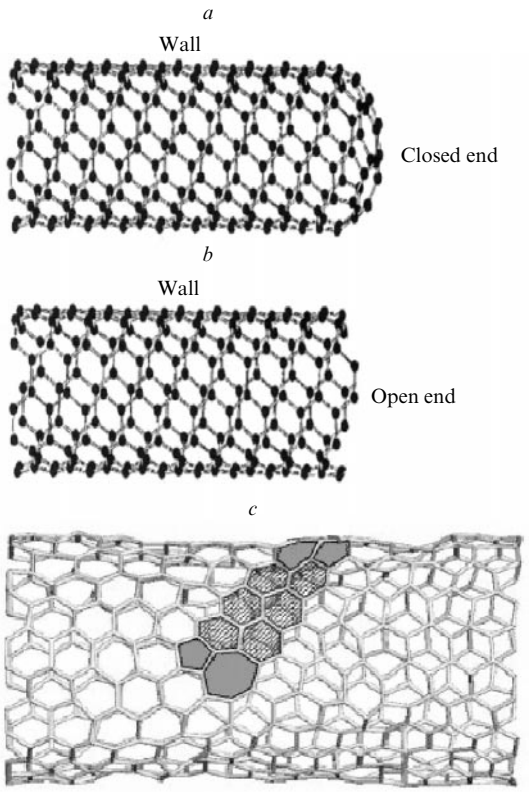


Figure 1. Schematic illustration of closed (*a*) and open (*b*) single-walled nanotubes and of a point defect that appears upon stretching of a carbon nanotube (*c*).[17]

As a rule, multi-walled nanotubes contain more defects than single-walled tubes. According to experimental and calculated data, defects of graphene layers can substantially affect the electronic, mechanical and chemical properties of nanotubes. Linear topological defects represent four-, five-, seven-, or eight-membered carbon rings present in the graphene layer in place of common six-membered rings. For example, when a nanotube is bent, a seven-membered ring is formed on its concave side and a five-membered ring is formed on its convex side. Mechanical or other impacts may produce point defects on the formed nanotubes. The example is the Stone–Wales effect that arises upon stretching of a carbon nanotube (Fig. 1 *c*).[19] It should be noted that the reactivity of straight nanotubes differs from that of bent nanotubes that bear topological defects.[20]

A unique feature of nanotubes with a high aspect ratio ($l/d \geqslant 1000$) and adequate electron conductivity is the presence of a maximally 'sharp' (of the order of magnitude of atomic sizes) edge on which very high electric field intensities are induced (10^3–10^4 V μm^{-1}) to generate the field (autoelectronic or tunnelling) emission of electrons. The fundamental and applied aspects of field emission to vacuum from carbon nanostructures (both pure and doped with different substances) were widely discussed in the literature.[21, 22] Undoubtedly, the interest in this problem was stimulated by the fact that the possibility of using nanotubes as the material for field-emission cathodes was demonstrated for a large number of laboratory models.[23–25] However, despite the high level of experimental instrumentation, the literature data on the effective use of different kinds of nanotubes are highly controversial. Apparently, this was caused by the high sensitivity of the structure of carbon nanomaterials with respect to minor nuances in their synthesis and also the strong dependence of emission characteristics on this structure. A certain problem is associated with the absence of clear conventional standards in the description of the subjects of study.

The structural properties of nanotubes (the presence of one or many layers, open or closed ends,‡ defectiveness, *etc.*), the preparation methods, and also the presence (or absence) of preferential orientation with respect to the support determine their efficiency in different application fields. For example, for vacuum cold emitters of current, single-walled carbon nanotubes demonstrated the record breaking values for the threshold potential difference of field emission onset (0.8–1.0 V μm^{-1}) and the emission current density ($\sim$4 A cm^{-2});[26] for multi-walled nanotubes substantially lower field emission currents were observed due to the lower electric field intensity as a result of small gaps between equipotential surfaces of coaxial graphene layers.

It should be noted that emission properties depend not only on the geometry of a particular nanotube, but also on its environment. It was found that the electric field on its end is screened by the neighbouring emitter if the distance between them is smaller than twice the size of the nanotube.[27] However, in the electrochemical applications of nanotubes, this effect is eliminated by the screening action of a polar electrolyte solution and, hence, it is not considered in this review.

Field emission is described by the Fowler–Nordheim equation that proclaims the superexponential dependence of the emission current (J) on the electric field (F):

$$J = AF^2 \mathrm{e}^{-(B\phi^{3/2}/F)}, \qquad (1)$$

where A and B are the constants depending little on the electric field; ϕ is the electron work function. Parameter F is related to the applied field intensity (V) by the expression

$$F \approx 0.2\frac{V}{r},$$

r is the characteristic radius of surface curvature.

The Fowler–Nordheim equation is plotted in the $\ln(JV^{-2})$ *vs.* V^{-1} coordinates. Its linearity suggests the tunnelling mechanism of electron emission; if the plot slope and its intersection points with axes are known, it is possible to determine the emitting surface area and the electron work function for a given V.[22] It is conventionally assumed that the Fowler–Nordheim plot is linear at low currents and deviates from linearity at higher V and J values due to the Ohmic potential drop in nanotubes.[28]

From the viewpoint of the majority of scientists (*e.g.*, see Refs 29, 30), it is the tips of carbon nanostructures that become the sources of electron emission upon application of electric field. For instance, studies on the electron emission from open and closed conical tubes formed by graphene layers made it possible to conclude [31] that electron emission from the outer edge of a conical tube end makes the main contribution to the emission current. This agrees with the data [32] that pointed out that the electric field becomes substantially stronger near the vertex of an open nanotube due to the wide scatter of the local field intensity, which determines the non-linear dependence of current in the coordinates of the Fowler–Nordheim equation.

‡ As a rule, the opening of nanotube ends is achieved during treatment with concentrated acids.

For samples containing elongated open nanotubes, the Fowler–Nordheim plot was also found to be non-linear.[33] Presumably, this confirms the fact that the limiting emission current cannot be described by the standard tunnelling theory. However, experimental studies produced linear $\ln(JV^{-2})$ *vs.* (V^{-1}) dependences.[34, 35]

It is generally accepted that the source of autoelectronic emission in a carbon nanostructure is its tip in the vicinity of which the field intensity reaches its maximum; however, as was assumed in a review, [22] the nanotube side surface can also serve as an effective emitter. For certain nanotube orientations with respect to the external electric field, the contribution of the emission from the side surface to the total current may be decisive, because the side surface considerably exceeds the tip surface.

At the same time, it was stated [36] that (i) emission is realised by a limited number of centres of relatively small sizes; (ii) to achieve agreement between the experimental dependences of emission current from carbon nanostructures on the external electric field and those calculated using the Fowler–Nordheim theory, the field strength should be several orders of magnitude higher than its conventional (used in the experiments) values and the electron work function should be lower than the generally accepted value; (iii) emission current from carbon nanotubes normal to the electric field vector is higher than the current from tubes parallel to the external field direction.

Furthermore, an original theoretical model was proposed [36] that allows one to describe the mechanism of autoelectronic emission. According to this model, the work function decreases due to the local internal field that arises as a result of a temperature gradient in carbon nanostructures based on a combination of graphite-like (sp^2-hybridised carbon atoms) and diamond-like (sp^3-hybridised carbon atoms) phases. The temperature gradient appears as the current flows through the sp^2- and sp^3-phases, with the latter phase acting as the cooler.[37] Constructing quantum mechanical models for charge and electrostatic potential propagation along a single-walled nanotube in the course of field emission has shown [38] that the field intensity increases at the nanotube ends. According to calculations, the potential barriers at side walls are much wider and higher as compared with the nanotube vertices for which the minimum parameters of the emission energy barrier were determined. The barrier lowering that leads to a considerable increase in the tunnelling current was caused by the penetration of the external field to the ends of structures under study.

Thus, the brief survey of publications presented above shows that the majority of researchers assumed the high emission current from carbon nanostructures to vacuum to be largely caused by the surface morphology peculiarities, namely, the presence of spikes and defects that lead to the appearance of areas with the atomic curvature radii. In several studies, the height and width of the potential barrier for the electron escape from nanotubes was observed to decrease in the presence of adsorbed atoms and molecules including water on the emitting surface.[39–46]

In our opinion, the mentioned peculiarities of the morphology of nanostructured carbon together with its unique electron structure should also be reflected in the electrochemical characteristics of materials so that the latter should differ in principle from those of ordinary carbon materials. This non-obvious assumption can be substantiated by the following experimental facts. When studying photoemission at the metal–electrolyte interface, it was unambiguously established that the electron work function to condensed media is substantially lower than to vacuum. Particularly, for aqueous electrolyte solutions, it decreased by 1.5–2.5 eV depending on the electrode potential (E) (for all metals, the electron work function to condensed media was $\sim$3.5 eV at the potential $E = 0.0$ V *vs.* SCE and linearly decreased as the potential shifted to the cathodic region).[47, 48]

It was also shown that photoemission properties of electrodes based on SWNT and metal electrodes are similar, namely, in both cases the photocurrent *vs.* potential dependence was described by an exponential dependence with an exponent of about 2.5. This means that for electrodes based on SWNT, as for metals, the work function decreases by 2.0 eV at $E = 0.0$ V *vs.* SCE and, above all, continues to linearly decrease as the potential shifts further to the cathodic region.[49]

On the one hand, if we assume that at the nanotube–solution boundary (analogously to the nanotube–vacuum boundary) the height and width of energy barrier of electron escape becomes smaller on atomically sharp sites of nanostructures, then a combination of this effect with the substantial reduction in the electrode potential-dependent work function gives rise to considerable tunnelling currents of electron transfer to solution in the cathodic region. On the other hand, in the majority of cases, the overpotential of an irreversible two- (or multi)-electron reaction is due to the formation of high-energy intermediates in the stage of heterogeneous transfer of the first electron.[50] However, for the tunnel transfer, the highly reactive solvated electrons (e_s^-) appear in solution. Alternatively, electrons are directly transferred to the acceptor molecules near the electrode surface area with high curvature. In other words, there is a possibility for generation of radicals and radical ions without a stage of formation of their high-energy precursors. In this case, the mechanism of electrode reactions radically changes.

Considering the anodic potential region, it can be concluded that the peculiarities of the electronic structure of nanotube materials, *viz.*, the presence of vacant electron states, may accelerate the electrode process in oxidation reactions as well.

III. Electrode reactions on nanotube electrodes

One of the first studies on the electrochemistry of nanotube materials appeared in 1996.[51] Since that time, the number of publications devoted to electrochemistry of carbon nanotubes progressively have increased. According to the information retrieved from a database,[52] the total number of publications on the electrochemistry of nanostructured carbon in 10 years exceeded 1800, which includes more than 90 reviews. Figure 2 shows the distribution of publications over years. On the other hand, the number of publications on nanotube electrodes is smaller than the number of publications on electrochemistry of fullerenes (in the first 10 years of their investigations, the number of publications exceeded 2000).[53] This could be caused by the fullerene characteristics more advantageous from the viewpoint of electrochemistry, namely, their strictly definite molecular structure, solubility in organic solvents, the vast number of chemical derivatives, and also the unique properties of fullerenes as depolarisers.

According to the diagrams of distribution of publications over lines of research for the first 100 studies and for 2007 (Fig. 3), the keenest attention was drawn to studying electrochemical kinetics and electrocatalysis, which was

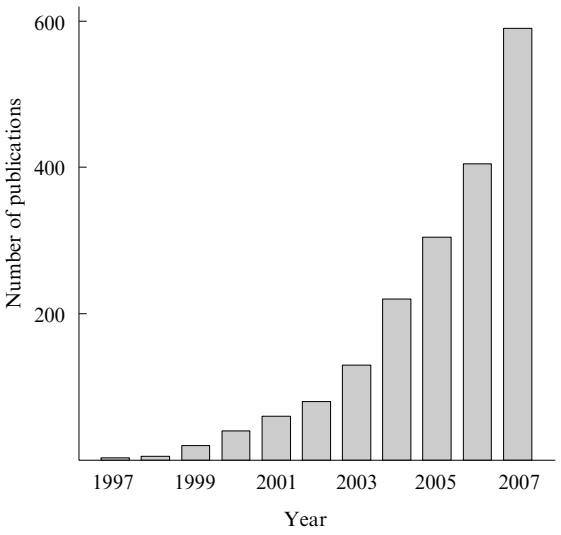


Figure 2. Distribution of the number of publications devoted to electrochemical studies of carbon nanostructures over years.[52]

followed by publications on the use of nanotube electrodes as sensors mainly for bioelectrochemical applications. Several reviews[54–58] can be considered as the most comprehensive recent publications in this field. The decrease in the fraction of publications devoted to hydrogen storage, lithium batteries and supercapacitors, *i.e.*, the subjects that dominated in 2001–2002, deserves mention. Probably, this is associated with the fact that the acceptable specific characteristics were already attained for carbon materials without using nanotubes of different morphology and also with the solution of scientific problems that have preceded the practical application of nanotubes.[59,60] At the same time, the studies on the use of carbon nanotubes in fuel cells and on the development of polymer–carbon nanostructured composite materials with high conductivity are quite topical, and the number of publications in this field increases.[61–64]

Apparently, the first study[65] on the electrochemical behaviour of a nanotube electrode dealt with poorly characterised multi-walled nanotubes with the length of ~ 5 μm and the diameter of ~ 200 nm. Cyclic voltammetric curves (CV) of $Ru(NH_3)_6^{3+}$ reduction on a nanotube electrode and cylindrical microelectrodes turned out to be very similar. This was taken into account when concluding that the electrochemical properties of the nanotube side surface are similar to those of amorphous carbon. The voltammetric curves were very close to the ideal 'Nernstian' form. In one study,[66] bunches of MWNT ($d \approx 30$ nm, $l \approx 3$ μm) in the form of porous columnar structures were used as electrodes for studying the redox reaction of potassium hexacyanoferrate (the standard test for the system reversibility), which is widely used in exploring the electrochemical properties of different carbon electrodes for which the $Fe(CN)_6^{3-/4-}$ redox pair is close to the ideal reversible system. The difference between CV peaks was 0.059 V (for comparison, on smooth platinum, this difference was 0.088 V) and did not depend on the potential scanning rate (v) in the range from 0.02 to 0.5 V s^{-1}. This entirely corresponds to a reversible process with a very high rate constant $k_0 \approx 0.5$ cm s^{-1} (Fig. 4). It is believed,[66] that this is the maximum value for all carbon materials studied so far. It was assumed that such a high rate of electron transfer (ET) was due to the presence of vacant electron states in nanotubes (the presence of such states makes easier the reagent oxidation).

The similar reversible mechanism of the electrochemical reaction of the $Fe(CN)_6^{3-/4-}$ pair was observed[67] on electrodes containing sparsely arranged multi-walled carbon nanotubes ($l \approx 8$ μm, $d \approx 100$ nm, the average distance between

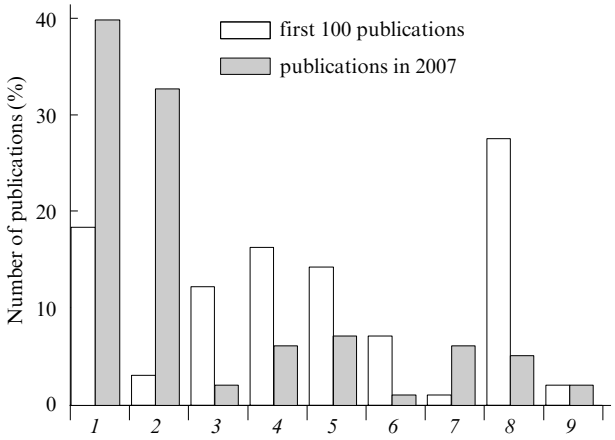


Figure 3. Distribution of publications over subjects.[52]
(*1*) Kinetics, electrocatalysis; (*2*) sensors; (*3*) hydrogen accumulation; (*4*) synthesis, coatings, films; (*5*) supercapacitors; (*6*) studies of physical properties; (*7*) fuel cells; (*8*) lithium batteries; (*9*) other fields.

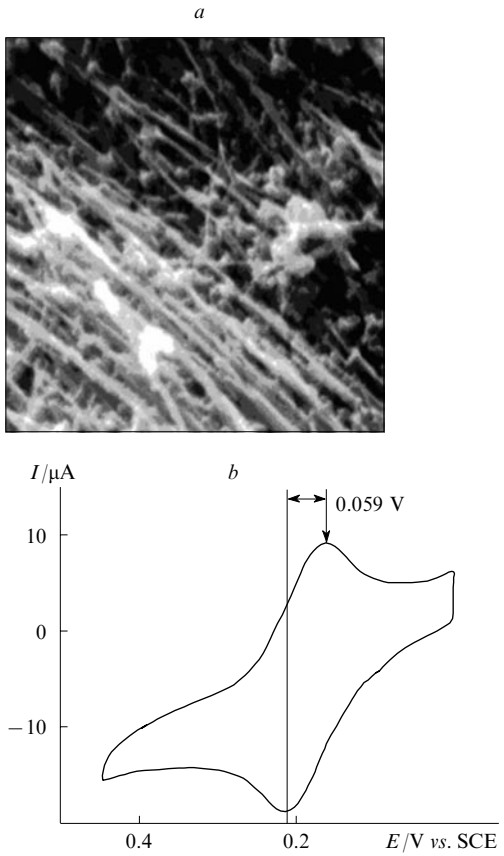


Figure 4. Electron microscopic image of MWNT ($d = 2–5$ nm, $l = 2–6$ μm) (*a*) and cyclic voltammograms of an electrode based on these MWNT (*b*).[66]
Electrolyte is a 5×10^{-3} M aqueous solution of $K_4Fe(CN)_6$.

nanotubes ~10 μm) oriented perpendicularly to the support. Presumably,[67] the extraordinary difference between the direct and reverse CV branches was caused by either the partial overlap of diffusion layers of individual nanoelectrodes or the incomplete hermeticity of the insulating layer between the electrolyte and the conducting support on which nanotubes are grown. Bearing in mind the relatively long distances between MWNT, the latter reason seems more probable.

In studies[68,69] on the electrochemistry of individual single-walled nanotubes carried out at a very high experimental level, the oxidation current of ferrocenylmethyltrimethylammonium ($FcTMA^+$) was recorded on the side surface of an individual well-characterised§ nanotube in aqueous solutions containing no supporting electrolyte. In this case, the current *vs.* potential curve for the reversible reaction deviated from the classical 'Nernstian' curve. In the potential scanning range used, the current did not reach the diffusion plateau, which delayed the wave (Fig. 5). The obtained results were well described by the Butler–Volmer equation with the rate constant for electrode reaction still higher than that reported in Ref. 66, namely, $k_0 = 4 \pm 2$ cm s^{-1}. A close k_0 value was obtained for the $FcTMA^+$ oxidation on a platinum nanoelectrode. No conclusion on whether such a high ET rate is intrinsic of the graphene sheet that forms the SWNT or due to its surface defects could be drawn.[68] It is of note that the current *vs.* potential curves were virtually the same for SWNT with the metal and semiconductor conductivity.

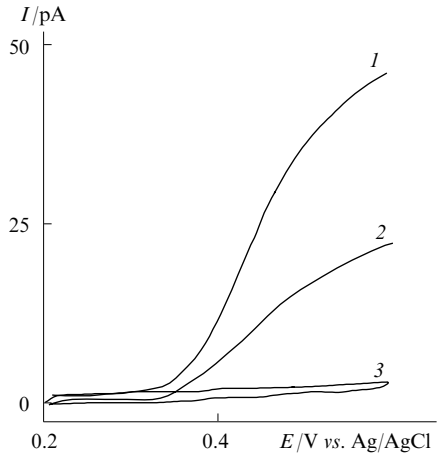


Figure 5. Voltammetric curves of individual SWNT with metal conductivity.[68]
Nanotube length 2 (*1*) and 1 μm (*2*); (*3*) control measurements in the absence of nanotubes under the same experimental conditions. Electrolyte is a 1.2×10^{-3} M aqueous solution of PF_6FcTMA.

The effect of the SWNT electronic structure on the dependence of the electron transfer rate on the applied potential was first theoretically considered by Dekker and co-workers.[68] The electron density of states for SWNT near the Fermi level (E_F) is relatively low, which leads to substantially longer gaps between the electron levels as compared with ordinary metals. When a potential is applied to the electrolyte–SWNT interface, E_F either increases or decreases, which changes the population of levels; moreover, the correlation between the potential variation and the corresponding shift of E_F can also deviate from linearity. As a consequence, a substantial part of the potential drop at the interface acquires the form of the chemical potential drop of the nanotube.

To describe the contribution of this drop into the total potential difference at the interface, the widely accepted model of two capacitors connected in series, *i.e.*, the electric double layer capacitance (C_{dl}) and the so-called quantum capacitance (C_q),¶ was used. Calculations of the rate constant for oxidation k_{ox} as a function of the potential within the framework of the Gerischer–Marcus model, carried out for two limiting versions, namely, the 'classical' $C_q \gg C_{dl}$ and the 'quantum' $C_q \ll C_{dl}$ cases, have shown that in the former case, the dependence is non-monotonic, although in both cases, its form is determined by the position of Van Hove singularities. Moreover, substantial differences in the kinetics of electrode reactions for SWNT with different diameters and different chirality were predicted. Particularly, calculations demonstrated considerable oscillations for k_0 in the Butler–Volmer equation as the nanotube diameter changed from 0.4 to 5 nm (Fig. 6). In connection with this, it should be noted that the experimental observa-

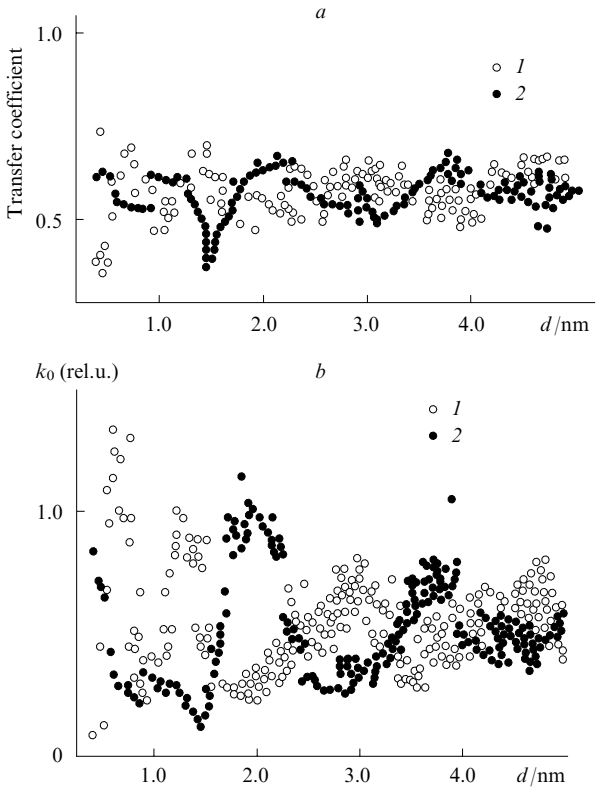


Figure 6. Calculated dependences of the transfer coefficient (*a*) and the standard rate constant (*b*) on the diameter of a SWNT with semiconductor (*1*) and metal (*2*) conductivity.[69]

§ The term 'well-characterised' means that the publication in question shows the majority of conventional characteristics of nanotubes, namely, a high-resolution image obtained with an electron microscope, the characteristic diameter and length, the state of their ends, the method of synthesis, the conduction type, the amount of impurities, the specific surface area.

¶ This term put forward in Ref. 70 in the theoretical consideration of two-dimensional metal was for the first time applied to semiconducting nanotubes in Ref. 71.

tions of this effect are hardly possible due to the difficulties of regulating the SWNT diameter over such a wide interval. The same holds for the difference in electrochemical characteristics between SWNT with the metal and semiconductor conductivities. It was noted that despite the noticeable deviation of the calculated $k_{ox}(E)$ dependences, this is insufficient for the direct experimental determination of the nanotube conduction type. The ET rate is directly related to the position and population of electron levels of both the redox system in electrolyte and the electrode. Bearing this in mind, it was assumed that, in principle, during the voltammetric measurements in electrolyte solutions, the densities of states of SWNT may differ by $\sim kT$. However, the experimental observation of CV peculiarities is only possible for redox systems when the following conditions are fulfilled: fast mass transport compared with ET and potential variations over a wide range.

The electrochemistry of electrodes based on precipitates from solutions containing dispersed nanotubes was studied.[72–75] The precipitate contained well characterised SWNT that formed nanopaper. Electron microscopic studies have shown that the mentioned nanopaper represented a substance containing single-walled nanotubes with the characteristic diameter of 1.2–1.4 nm, which were stuck together under the action of van der Waals forces to form bundles (of $\sim$30 nanotubes) with the ribbon structure. These bundles formed coarser aggregates measuring up to several hundred micrometres and looking as carpets. The specific capacitance and the surface density of nanopaper were 30–35 F g^{-1} and 0.3–0.4 mg cm^{-2}, respectively. The undeniable merit of nanopaper electrodes is the absence of a support and, as a consequence, no need for providing electric contact between it and nanotubes. Impedance measurements have shown that the dependence of the differential capacitance of nanopaper on the measuring frequency somewhat differed from the analogous dependence measured on the graphite basal plane. The deviation was caused by the porous structure of the electrode. For such electrodes, the voltammetric and impedance measurements carried out in water, organic solvents, water–organic mixtures and ionic liquids have shown that the shape of voltammetric curves and the electrode capacitance depend weakly on the nature of inert supporting electrolyte, namely, the charges of its ions, hydrophobicity and its mass. At the same time, it is regretful that the depolariser electrooxidation and electroreduction were beyond the scope of these studies.

Recently, studies that involved modification of electrodes by combining carbon nanostructures with different biocompounds deposited on the surface of a conducting support have been actively developed with the aim of enhancing the selectivity, catalytic activity and biocompatibility of the latter.[76–79] Thus, several electrochemical biosensors based on carbon nanotubes were developed, which demonstrated that it is, in principle, possible to determine superlow concentrations of biomolecules. The use of such biosensors is promising for medicinal and environmental purposes.[76,77] This kind of information on the characteristics of biosensors for determination of compounds such as glucose, dopamine, phenol derivatives, organophosphorus pesticides, hymecromone, *etc*., can be found in Refs 78 and 79. Biochemical modification makes easier the selective ET between active centres of biocompounds and the modified nanostructured electrode. As a typical example, Fig. 7 shows a rather complicated scheme of glucose oxidation to

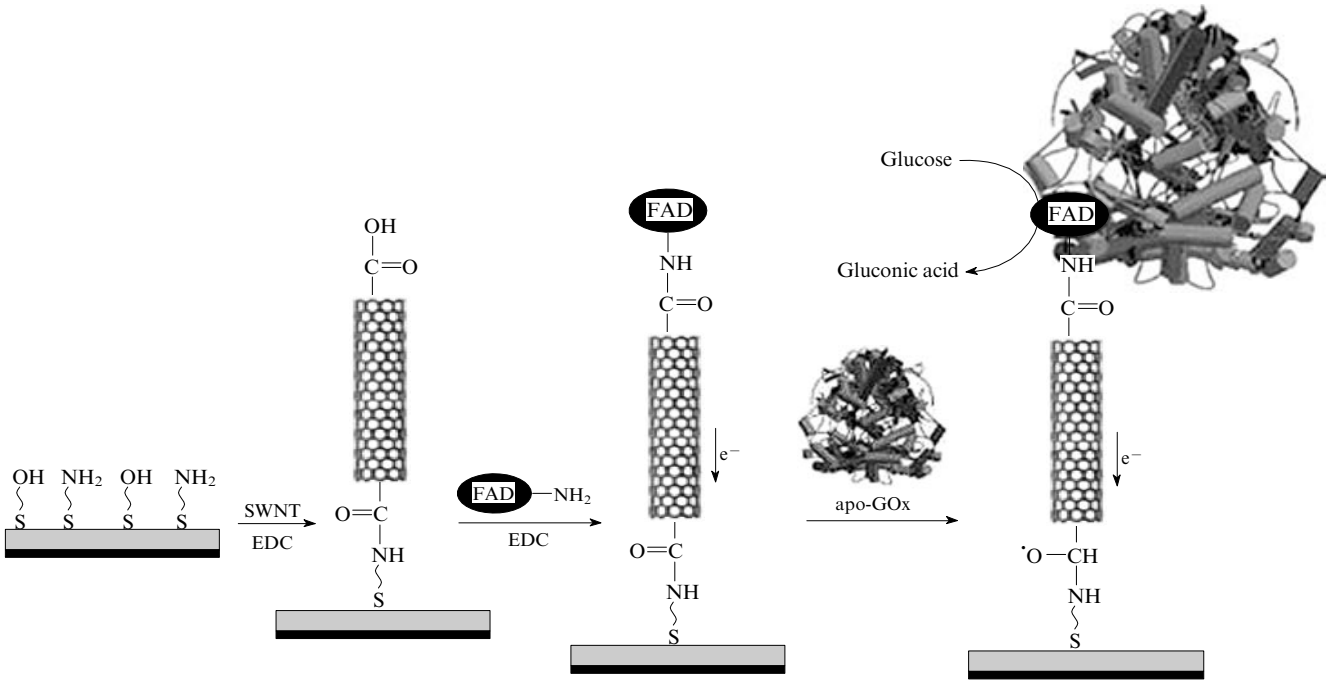


Figure 7. Scheme of preparation of an electrode based on SWNT modified with apo-glucoseoxidase (apo-GO_x) and of oxidation of glucose on it.[58]

On the surface of a gold electrode, a monolayer of a mixture of 2-mercaptoethanol and cysteamine in the 3 : 1 ratio was deposited, which enabled coupling with single-walled carbon nanotubes in the presence of 1-ethyl-3-(dimethylaminopropyl)carbodiimide (EDC) hydrochloride. Then, amino derivatives of the flavin adenine dinucleotide (FAD) co-factor were attached to the carboxyl groups located at the ends of single-walled nanotubes. It is on FAD elements that glucose oxidation reaction occurred.

gluconic acid on a modified electrode based on carbon nanotubes.[58]

Analysis of the literature has shown that in the majority of studies attention was focused on the EO of different compounds on electrodes modified with nanotubes in the anodic potential region.[80–87] Glassy carbon (GC) was used most often as the support for such electrodes. Moreover, CV recorded on GC were used as the reference in analysing the obtained results. As a rule, the modification consisted of the deposition of a suspension of nanotubes preliminarily dispersed in some organic solvent onto a support. Thus the use of multi-walled nanotubes dispersed in dihexadecyl hydrogenphosphate (DHP) allowed the oxidation of 10-hydroxycamptothecine (HCPT) in aqueous perchloric acid to be detected on a GC support.[80] It deserves mention that the appearance of a clear peak of HCPT oxidation in a differential pulse voltammogram was only observed when electrodes based on carbon nanotubes were used (Fig. 8). The authors of the above study failed to give any unambiguous explanation for this effect but only pointed out the high specific surface, peculiar electronic structure and strong adsorbability of MWNT.

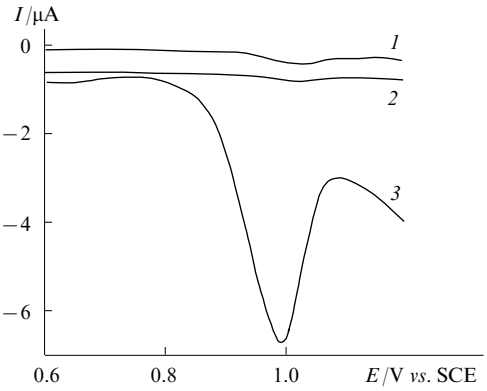


Figure 8. Differential pulse voltammetric curves of 5×10^{-7} mol litre^{-1} HCPT in 0.5 M $HClO_4$ on different electrodes.[80] (*1*) GC electrode; (*2*) GC electrode modified with a DHP film; (*3*) GC electrode modified with a MWNT-DHP film.

The analogous electrocatalytic properties of multi-walled nanotubes oriented normally to the support were demonstrated for the oxidation of several other compounds.[81,82] It was shown[82] that selective oxidation of glucose in aqueous alkaline solutions on MWNT ($d \approx 200-400$ nm, $l \approx 10$ μm) occurs at much lower overpotentials (by $\sim$0.4 V) as compared with a GC electrode (Fig. 9). A bright example of the electrocatalytic effect of carbon nanostructures are the EO reactions of norepinephrine and ascorbic acid that proceed at substantially lower potentials as compared with a pure GC electrode.[83,84] A substantial decrease in the overvoltage (by $\sim$0.9 V) of hydrogen sulfide oxidation on carbon nanotubes ($d \approx 20-40$ nm, $l \approx 1-5$ μm) as compared with a GC electrode was noted.[85]

The electrocatalytic effect of selective oxidation of guanine and adenine on carbon nanotubes modified with β-cyclodextrin was revealed.[86] It was assumed that such a modification leads to the formation of a three-dimensional network structure capable of concentrating guanine and adenine at its interface. As a result, the EO current of these

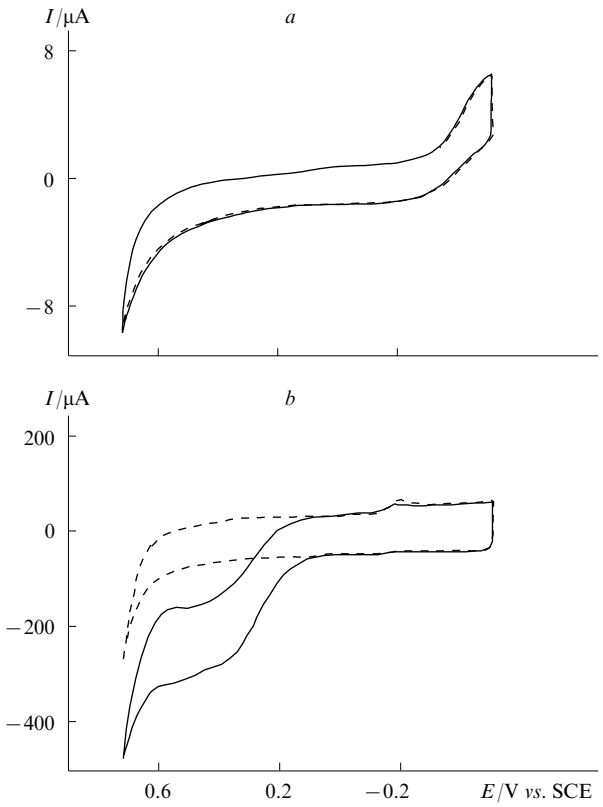


Figure 9. Cyclic voltammetric curves on GC (*a*) and MWNT oriented normally to a GC support (*b*).[82]
Dashed lines show the changes in the supporting electrolyte solution. Electrolyte contained a 3×10^{-2} M solution of glucose + 0.10 M NaOH.

compounds substantially increased and this allowed their detection limit to shift down to 0.1–0.2 μg ml^{-1}. Electrooxidation of glutathione on oriented carbon nanotubes was studied by cyclic and square-wave voltammetric techniques.[87] Cyclic voltammograms recorded in a glutathione-containing solution and on electrodes formed by nanotubes oriented normally to the support differed in principle from those recorded on a GC electrode (Fig. 10). Based on this fact, it was stated that glutathione can be analytically determined on such electrodes.

Recently, attention was also drawn to modification of nanotubes themselves by the deposition of catalytically active metals on their surfaces.[88–100] Such composite materials were used most often in studying the oxidation reactions of organic substances as applied to the development of electrodes for fuel cells. Methanol oxidation at low anodic potentials on sulfonated carbon nanotubes modified with platinum was reported.[88] The substantially higher electrocatalytic activity of electrodes of platinum-modified sulfonated nanotubes as compared with the electrodes of the same design based on pure nanotubes and platinum was shown. This experimental result was associated with the presence of sulfo groups on the surface of carbon nanostructures.

The higher oxidation currents and the lower overpotentials observed in the oxidation of procaine and nitrite ions on modified carbon nanotubes were associated[89,90] with the increase in the effective surface area due to the strong adsorption of depolarisers on carbon nanostructures. The

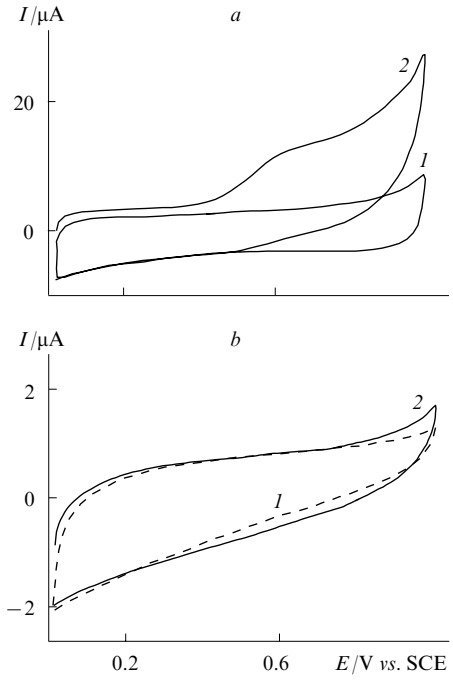


Figure 10. Cyclic voltammetric curves on oriented MWNT (*a*) and GC (*b*) in 0.05 M phosphate buffer (pH 7.0) in the absence (*1*) and in the presence of 8×10^{-3} mol litre^{-1} glutathione (*2*).[87]

analogous conclusion was also drawn in Refs 91 and 92. Thus the electrocatalysis of hydrogen EO was attributed[91] to the nickel plating of multi-walled nanotubes. In connection with this, attention should be drawn to a study[93] in which platinum was deposited only on the MWNT open ends and the defects that appeared upon their mild oxidation. Platinum deposits which were considered as nanoclusters (average diameter of $\sim$120 nm) had a mushroom shape and consisted of Pt grains with the characteristic diameter of $\sim$13.0 nm. The high catalytic activity of multi-walled nanotubes modified with platinum nanoclusters was demonstrated for oxygen reduction and methanol oxidation. The promotion of the listed reactions and also the lowering of the overpotential of methanol reduction were explained by not only the higher effective surface of platinum and its catalytic activity, but also by the synergistic effect of the Pt/MWNT composite.

In a later publication,[94] the nucleation on defects formed as a result of doping of carbon nanotubes with nitrogen allowed synthesising platinum nanoclusters with the characteristic size $d \approx 2.8$ nm. Nanotubes were preliminarily grown on a carbon tissue, which ensured easy electron transfer between the tissue and platinum nanoclusters and, as a consequence, the superhigh catalytic activity of this electrode in the methanol EO. These results agree with the data[95] on the higher catalytic activity upon incorporation of platinum particles ($d \approx 3.6 \pm 0.6$ nm) into nitrogen-doped MWNT ($d \approx 200$ nm, $l \approx 40-50$ μm) oriented normally to the support as compared with platinum deposited on non-doped nanotubes and also with pure carbon nanotubes. For Pt–Ru nanoparticles ($d \approx 4.8$ nm) deposited on the nanotube surface, the high electrocatalytic activity in the methanol oxidation was demonstrated.[96] A similar catalytic effect was observed for the MWNT surface modified with palladium nanoparticles.[97] The best electrocatalytic characteristics in methanol EO were achieved[98] for Pt–Ru particles ($d \approx 7.7$ nm) deposited on a defect-free (in contrast to reported data[94,95]) surface of MWNT ($d \approx 20-50$ nm, $l \approx 10$ μm).

For methanol electrooxidation and oxygen electroreduction, the higher catalytic activity of Pt/SWNT/GC electrodes as compared with a Pt/C/GC electrode was observed.[99] Electrooxidation of ethylene glycol on MWNT modified with Pt and Pt–Ru nanoparticles was studied.[100] It was shown that in this case, the catalytic activity sharply increases with the deposition of metal particles on carbon nanotubes.

Thus, this research field is rapidly developed towards the practical application of results. In many studies, the particular designs of electrodes for fuel cells were proposed. All the authors pointed out the unique catalytic characteristics of composite electrodes prepared by similar processes, namely, by the deposition of nanosize catalyst particles onto carbon nanotubes. However, it is generally agreed that the role of nanotubes as such is reduced to the generation of sites for nucleation of catalyst nanoparticles and providing adequate current supply to these particles. The peculiarity of nanotubes manifests itself only in the fact that the deposition of catalysts starts on atomic defects on their surface, *i.e.*, the metal nanoparticles with the characteristic size of $\sim 2-4$ nm are incorporated into the graphene sheet. Moreover, according to Ref. 98, the morphology of the nanotube surface affects the ratio of components upon deposition of Pt–Ru particles. After the deposition of the catalyst, the nanotube surface plays no independent role in electrode reactions.

The electrocatalytic effect was associated[101] with the presence on the nanotube surface of active functional groups (hydroxyl, carboxyl, *etc.*) that behave either as ligands with respect to the compounds to be determined or facilitate the electron transfer due to the formation of hydrogen bonds. The same conclusion was made by the authors of publications[102,103] who assumed that the electrocatalysis of the oxygen and nitrobenzene reduction on nanostructured carbon electrodes was caused by the presence of functional groups on their surface. At the same time, as was noted in a review,[104] for nanotubes with the larger number of functional groups formed upon their modification on their ends and walls, the higher ET rates were observed, whereas the adsorption processes did not play any significant role.

Original electrodes consisting of nanopaper based on smooth carbon nanofibres ($d \sim 10$ μm) were developed and studied.[105] Their surfaces were used as the supports for growing MWNT perpendicularly to them. It was shown that the current density of $K_4Fe(CN)_6$ reduction on such electrodes increased after the latter were electrochemically oxidised in a solution of nitric acid (Fig. 11). In addition to increasing the electrochemical activity, the MWNT oxidation increased the specific surface area and the capacitance, namely, from 71 to 208 m^2 g^{-1} [measured by the Brunauer–Emmett–Teller (BET) method] and from 19 to 165 F g^{-1}, respectively, and also changed the hydrophobic nature of the electrode surface to hydrophilic. Presumably, this was caused by the formation of functional groups on the MWNT surface upon oxidation, although the data from high-resolution X-ray photoelectron spectroscopy reported in this study did not confirm this suggestion. At the same time, the data obtained by the BET method unambiguously show that the MWNT surface structure changed with

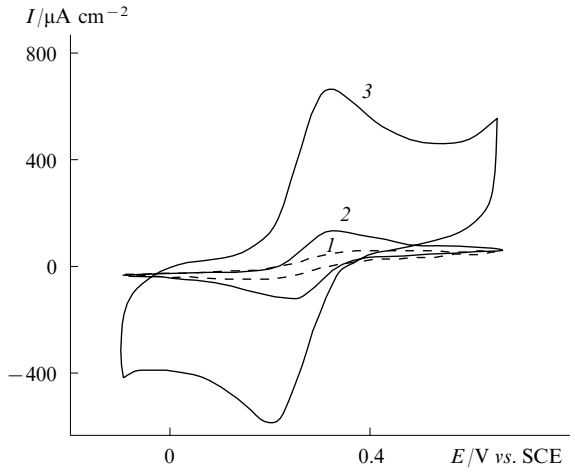


Figure 11. Cyclic voltammetric curves on different electrodes in 10^{-3} M $K_4Fe(CN)_6$ + 1 M KCl solution.[105]
Electrode material: (*1*) nanopaper of carbon fibres, (*2*) nanopaper with grown MWNT, (*3*) sample *2* electrochemically oxidised in nitric acid. Potential scanning rate 0.02 V s^{-1}.

oxidation and the pore size decreased from 2.6–6.0 to 1.4–3.0 nm.

In line with the aforementioned, it should be noted that, by definition, the reaction overpotential cannot depend on the electrode surface area, and its relationship with the specific surface claimed by certain authors seems improbable. The same is true for the relationship between the electron transfer rate and the surface density of functional groups, obviously, in the absence of interaction between the latter.

In contrast to the authors mentioned above, many scientists believe that in addition to topological defects the peculiar electronic structure of nanotubes can be the reason for the higher electrocatalytic activity of nanotube electrodes as compared with electrodes containing no carbon nanoforms. It was assumed that the main contribution to such properties was made by the open ends of nanotubes rather than by the defects on their side walls.[106–110] In one of these studies,[106] attention was drawn to the fact that the treatment of carbon nanotubes with acid not always results in their functionalisation. Particularly, it was found that nanotubes treated with nitric acid contained virtually no functional groups on their surfaces, as was clearly demonstrated by voltammetric curves and the results of X-ray photoelectron spectroscopy. It was stated that the presence of oxygen-containing functional groups did not increase the rate constants for the redox reaction of potassium hexacyanoferrate and the electroreduction of ruthenium hexaammine trichloride so that the main reason for the electrochemical activity of MWNT was the presence of topological defects located on the ends and walls of nanotubes. Presumably, the number of defects increased upon the break or rupture of structures (which contradicts the conclusion made in Refs 104, 105). A similar idea was put forward later (Ref. 107), where the electrocatalytic activity of SWNT-based electrodes in the $Fe(CN)_6^{3-/4-}$ redox reaction was revealed. It was assumed that the surface of single-walled nanotubes contains many defects, namely, five-membered rings on nanotube vertices and defective pairs five-membered–seven-membered rings on their side surfaces. Moreover, the high surface curvature favours the surface activation. It is due to the presence of such defects that the electron transfer between nanotubes and a redox-centre localised in solution becomes easier.

Owing to their special electronic structure, single-walled nanotubes can serve as a 'molecular wire', which quickly delivered the electrons to the centre of the reaction complex. It was also assumed[106] that the high surface density of topological defects is the source for the substantial electrocatalytic activity of nanostructures.

The electrochemical behaviour of an electrode built of short open SWNT ($d \approx 1.1-1.2$ nm, $l \approx 20-100$ nm, surface concentration $\sim 10^{13}-10^{14}$ cm^{-2}) oriented normally to the support and modified by acid treatment was studied.[108] The tubes were attached through amide bonds to the insulating monolayer of 11-amino-n-undecanethiol (AUT) deposited on a gold support (Fig. 12). Despite the presence of an insulating layer between SWNT and the gold support, the dependence of CV curves on v for such an electrode was well described in terms of an equivalent circuit with the 'tunnelling' resistance of the insulating layer used instead of the solution resistance. Presumably, the presence of a π-conjugated system in the skeleton of a single-walled nanotube allows the latter to act as both an acceptor and a donor of electrons and also to maintain ET between a redox pair in solution and the gold electrode. For instance, in a cathodic process, a single-walled nanotube accepts electrons from gold atoms thus increasing the Fermi level energy of SWNT, which leads to the donation of electrons to the redox pair. It was noted that the specific electronic structure of SWNT, which manifests itself in a large number of occupied and vacant electron states, not only determines the fast electron transfer between the nanotube and a redox pair, but also makes easier the electron tunnelling between SWNT and the support. However, the facilitation of ET at the nanotube–solution interface was not assigned to the presence of functional groups.

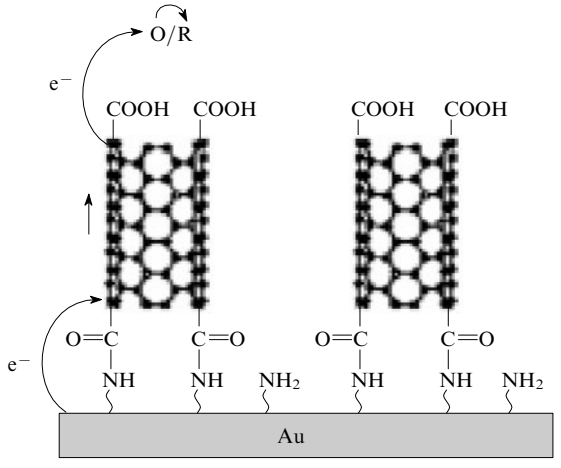


Figure 12. Illustration of electron transfer from an Au/AUT/SWNT electrode to a redox centre O/R.[108]

In a review,[109] the acceleration of electron transfer on carbon nanotubes was explained by two factors, namely, good wettability of the electrode (due to the porous structure of nanotube bunches) and the peculiar electronic structure of the surface graphene layers that form nanotubes, which is characterised by such properties as chirality, low dimensionality and topological defects. It was also

assumed that the higher electrocatalytic activity was manifested by the ends of carbon nanotubes rather than by their side walls. This is consistent with the theoretical conclusions [110] on the strong dependence of capacitance characteristics of a graphene ribbon on the shape of its edges. Presumably, due to the edge effects, the electron density of states of a graphene ribbon can substantially change even at a moderate applied potential.

The number of studies devoted to the electroreduction of compounds on nanostructured carbon was considerably smaller than those dealing with electrooxidation. Some authors also explained the qualitative changes in the electrode reaction conditions in terms of the higher specific surface area and the larger number of functional groups when nanotube electrodes are used.

The easier electron transfer from the nanotube surface to a depolariser in the cathodic potential range [111–115] as well as the lower overpotential of hydrogen peroxide reduction on electrodes modified with multi-walled carbon nanotubes [116] were explained by the increase in the effective specific surface of electrodes, the presence of charged functional groups and adsorbed molecules on the surface of carbon structures and also by the specific electronic structure of nanotubes themselves. The high characteristics of such electrodes were caused by the synergistic effect of these factors.[117,118] Studies on carbon nanotubes ($d \approx 10-500$ nm) deposited on a GC support have shown that the electrolyte penetrated into the space between fibres, which favoured the increase in the specific capacitance up 60 F g^{-1} and the generation of high faradaic currents.[119] Thus the current : capacitance ratio for nanofibres was three-times higher than for a GC electrode. The results of BET measurements presented in the latter study have shown that the nanofibre surface accessible for gas molecules (N_2) was considerably smaller that the surface accessible for the electrolyte solution.

At the same time, many scientists associated the easier ET with peculiarities of the surface structure of nanostructured carbon. Thus the lower overpotential of depolariser reduction, particularly, the oxygen electroreduction at low potentials on a modified nanotube film, was explained [120] by the presence of special formations with the nanoscale diameter based on graphene sheets that exhibited a peculiar electronic structure and contained topological defects of their surface.

Mention should be made of studies [121,122] on the electrochemical properties of multi-walled nanotubes ($d \approx 40-60$ nm, $l \approx 40-50$ μm, density of distribution $\sim 2 \times 10^4$ cm^{-2}) oriented normally to the support and subjected to the plasma treatment with argon and hydrogen ions with the aim of creating defects in their structure. Raman spectroscopic studies have shown that argon ions were incorporated into the graphene lattice so that the nanotube surface became charged to form defects with electron-withdrawing properties that cause shortening of sp^2-bonds. In contrast, treatment of MWNT with hydrogen ions resulted in closure of dangling bonds, *i.e.*, a sort of 'healing' of defects, which led to the disappearance of reaction sites from the surface. By the example of studying the $Fe(CN)_6^{3-/4-}$ redox pair, it was shown that the electrode reactions on nitrogen-treated MWNT were characterised by the reversible-quasireversible kinetics, whereas the hydrogen treatment led to MWNT passivation, which resulted in irreversibility of the electrode reactions with the difference between $Fe(CN)_6^{3-/4-}$ electroreduction and electrooxidation peaks approaching ~0.24 V. Presumably, the knowledge of the nature of the carbon nanotube defects would allow one to relate them to the mechanism of electrochemical processes. It was concluded that the electrocatalytic activity of nitrogen-doped MWNT is substantially higher as compared with pure nanotubes.[95]

According to certain data,[123] the formation of defects in nanotube films by treating them with ozone led to a sharp decrease (from 88.4 to 9.4 Ω cm^{-2}) of the charge transfer resistance for the reduction of triiodide ions. It is of note that this result resembles those obtained when studying the effect of doping with nitrogen and boron on the emission characteristics of nanotubes. In both cases, the substantial reduction in the work function was observed (for example, for nanotubes doped with boron, by ~1.7 eV) and, as a consequence, substantial enhancement of field emission parameters.[43,124,125]

It was shown [126] that functionalisation of MWNT proceeds most probably on their ends rather than on side walls and the specifics of functional groups localised on the nanotube edges determines the ET rate (in some cases, electrode reactions are accelerated). For example, for an SWNT-based electrode modified with dihexadecyl phosphate, the votammograms showed two clear peaks (at −0.39 and −0.93 V) of oxygen reduction in 0.1 M NaOH solution. On a GC electrode, the second peak was not observed at all (Fig. 13).

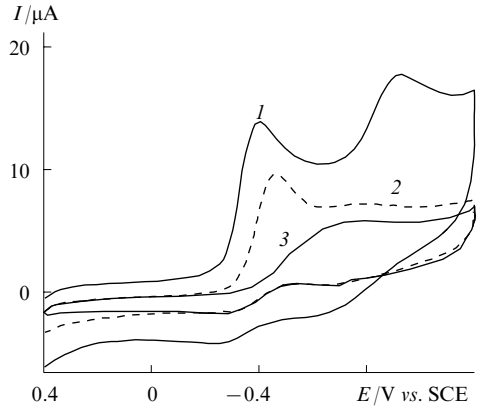


Figure 13. Cyclic voltammetric curves of oxygen reduction in 0.1 M NaOH solution on different electrodes.[120]
Electrode material: (*1*) GC modified with a SWNT-DHP film; (*2*) GC; (*3*) GC modified with a DHP film.

It was demonstrated [127] that if SWNT dispersed in different organic polyelectrolytes were deposited as a film on the surface of a GC electrode, such a modification made possible the effective determination of hydrogen peroxide at low working potentials. It was unambiguously concluded that the high electrocatalytic activity of ends of nanotubes oriented normally to the electrode surface rather than the high specific surface area of these electrodes was responsible for the decrease in the overpotential of H_2O_2 reduction on them. This agrees with the statement [128] that the electrochemical properties of electrodes modified with carbon nanotubes depend on the nanotube orientation.

It was shown experimentally that it is more advantageous to use bundles of oriented carbon nanotubes than randomly dispersed nanotubes. Taking this into account,

the former electrode version allows one to more effectively perform the electron transfer between carbon nanostructures and redox-active centres. This experimental observation is associated with the fact that for nanotubes oriented normally to the support, the electrons can travel between the conducting support and functional groups along a single nanotube. For randomly oriented nanotubes, two versions of electron transfer are probable. The first mechanism consists in hopping from one nanotube to another and, probably, through nanotube walls. Obviously, this way is more hindered as compared with the electron transport along a single nanotube. The second version appears to be similar to the process in a redox polymer where the diffusion of differently charged ions to the redox centre is the rate-determining step. However, from our viewpoint, the results of the latter study can be explained by the higher electrochemical activity of nanotube ends as compared with the side surface (which corresponds to the assumption made in Ref. 127) and also by the apparent improvement of the access of electrolyte and, hence, of reaction species to the ends for oriented nanotubes as compared with non-oriented.

It should be noted that the overwhelming majority of studies devoted to the reduction of various compounds were carried out on electrodes containing modified nanotubes. The results that confirm the peculiarities of electrode reactions on such structures were obtained in a cycle of studies.[129–134] However, in contrast to the previous studies, the CV current on a well-cleaned nanopaper electrode was observed to increase (Fig. 14 *a*) upon the addition of an acceptor of solvated electrons (N_2O) to the solution. The characteristics of SWNT and nanopaper prepared on their basis were close to those used in Refs 72–74. To remove the traces of surfactants from the SWNT surface, the samples were placed in water and irradiated with γ-quanta (a cobalt-60 unit) with the radiation dose of ~50 Mrad. This treatment led to a noticeable increase in the sample capacitance in low-frequency measurements and, hence, to the increase in the surface area accessible for electrolyte.[132] It should be noted that under the action of reactive radicals ($^{\bullet}OH$, $^{\bullet}H$) formed in water during the γ-radiolysis, the decomposition of organic impurities to H_2O and CO_2 occurs; however, no functional groups were detected on the irradiated nanotube surface by spectrophotometry (UV-Vis-NIR spectrophotometer for the ultraviolet, visible and infrared spectral ranges) and Raman spectroscopy.

Presumably, the increase in current upon addition of N_2O to the solution, which was entirely absent for a GC electrode, was not unambiguously determined by the trivial electroreduction of nitrogen(I) oxide on the surface of a nanotube electrode, because the current amplitude was virtually independent of the potential scanning rate variations in the range of $0.01-0.5$ V s^{-1}. This effect was explained by the injection of electrons to the electrolyte solution from sites with atomic sharpness on carbon nanostructures. The latter process leads to the formation of solvated electrons that are later trapped by N_2O molecules. Electrodes of filament and columnar carbon nanostructures were studied in a similar way. The former structure (see Fig. 14 *b*) represented a single-walled nanotube with the diameter of 2–4 nm, which was covered with a shell with the diameter of 50–130 nm consisting of disordered nanostructured graphite-like carbon.[135] In the latter case, according to electron microscopic data, nanostructured carbon consisted of columnar formations ($l \approx 2-3$ nm, $d \approx 50$ μm) oriented in parallel to the cathodic deposit axis (see Fig. 14 *c*). On the hemispherical vertices of these structures, MWNT were located ($d \approx 20-30$ nm, $l \approx 1$ μm) (see Fig. 14 *d*). For these structures, the presence of injection of solvated electrons at moderate cathodic potentials was also experimentally proved.

Figure 15 exemplifies dependences of the current density on the potential measured on the GC and columnar electrodes, for solutions containing poorly reducible NO_3^- ions. It is evident that on a columnar electrode the NO_3^- reduction was observed as soon as at $E \approx -1.0$ V; hence, the decrease in the overpotential due to the use of MWNT was ~0.9 V, which is comparable with the data[85] on the decrease in the overpotential of hydrogen sulfide oxidation on a nanotube electrode.

The relationship between the surface morphology and the electron emission current was revealed from voltammet-

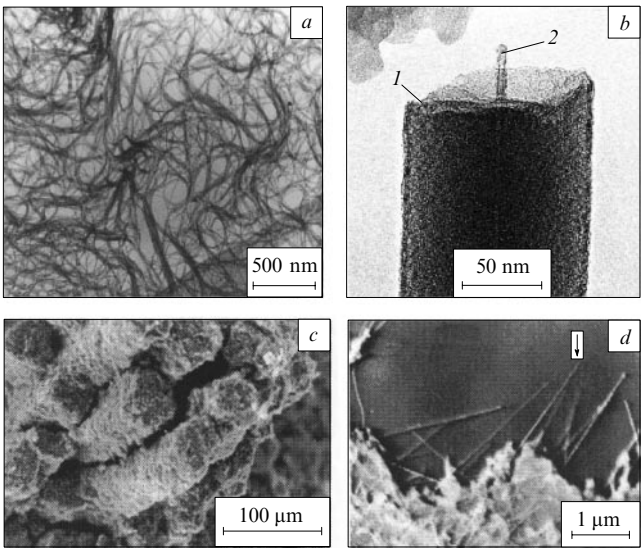


Figure 14. Scanning electron microimages of nanostructured carbon. (*a*) Nanopaper; (*b*) end of a nanofilamentary sructure, (*1*) outer shell, (*2*) inner single-walled nanotube;[135] (*c*) columnar structures; (*d*) a columnar structure vertex at high magnification.[136]

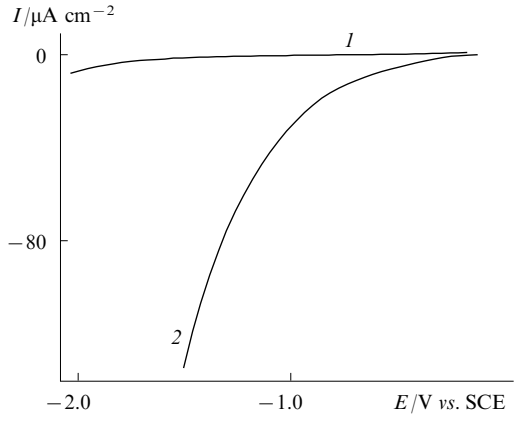


Figure 15. Current density of the reduction of NO_3^- ions on glassy carbon (*1*) and columnar (*2*) electrodes as a function of potential.[131] Electrolyte is 0.1 M Na_2SO_4 + 10^{-2} M $NaNO_3$. Potential scanning rate 0.05 V s^{-1}.

ric curves measured on an electrochemically sharpened tungsten electrode for which a decrease in the overpotential of electron emission as compared with polished metal electrodes was also demonstrated.[134] It should be stressed once more that in the presence of surface areas of high curvature the decrease in the electrode reaction overpotential was independent of the specific surface of electrodes used in several studies,[130–134] which changed from 8.0 $m^2\ g^{-1}$ for a columnar electrode to 600 $m^2\ g^{-1}$ for a nanopaper electrode, and the decrease in the electron emission overpotential for both structures as compared with smooth GC electrodes was in the range of 0.8–0.6 V.

The most convincing experimental evidence for the presence of electron injection at moderate cathodic potentials was obtained in hexamethylphosphorotriamide solutions (HMPA). In such solutions, the steady-state concentration of e_s^- can be obtained at room temperature. It was shown [133, 134] that the physical and chemical characteristics of HMPA solutions containing solvated electrons measured using nanotube electrodes in the range of moderate cathodic potentials completely coincided with those observed earlier (see Refs 137, 138) for the amission of electrons from smooth metal electrodes at high cathodic potentials.

Thus, irrespective of the physical nature of injection, which still remains unclear, the use of carbon nanostructures as the emitters of electrons opens up prospects for 'bypassing' the heterogenous reaction of transfer of the first electron. In this case, the electrocatalytic effect is due to the extremely high reactivity of solvated electrons that are involved in a heterogeneous reaction with many organic and inorganic substances with rate constants close to diffusion ones. As a rule, this gives rise to reactive intermediates, namely, radicals and radical ions, that are quickly reduced on the electrode at moderate cathodic potentials.

As to the injection mechanism, the most probable route is the tunnelling transfer of electrons under the barrier with the smaller width due to the higher surface curvature intrinsic to graphene sheets or due to topological defects on the side surface of carbon nanotubes.[139, 140] This viewpoint is confirmed by the results of studies [141, 142] in which a considerable tunnelling current of e_s^- formation was observed only on a nanostructured Ag electrode. However, the mechanisms associated with the so-called 'dissolution of electrons' from atomically sharp sites on the nanotube surface or with the tunnelling transfer of electrons to a reaction centre located in solution near a spike surface region cannot be ruled out. A similar effect was observed [141, 142] for non-equilibrium electrons that were formed when the electrode was heated by a picosecond laser pulse.

It should be noted that the decrease in the overpotential of the depolariser ER observed on nanostructured electrodes can easily be explained within the framework of an assumption on the injection of solvated electrons. Thus, the use of electrodes containing high curvature elements as the electron emitters changes the reaction mechanism, which is indeed a size effect in electrode kinetics. A similar consideration of different versions of size effects in electrochemistry was carried out in some reviews.[143, 144] The mentioned subject remains very topical and a vast number of studies devoted to the effect of the characteristic size of an electrode surface unit on its electrocatalytic properties have appeared since the publication of the reviews cited. As a typical

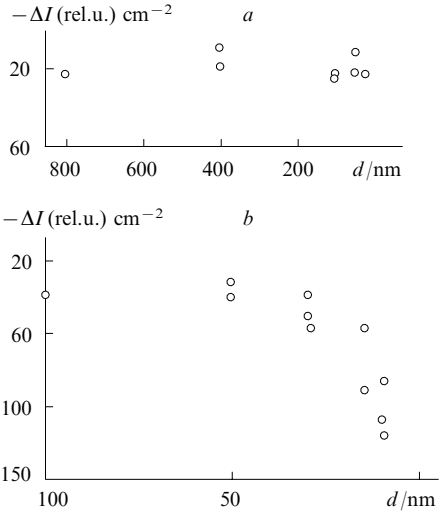


Figure 16. Dependences of the relative current density on the gold particle size in the intervals from 100 to 800 nm (*a*) and from 0 to 100 nm (*b*).[146]
Electrolyte 0.1 M KOH solution, $E = -0.8$ V *vs.* SCE.

example, mention should be made of publications [145, 146] in which the critical particle size that corresponds to the maximum electrocatalytic activity of an Au electrode was determined. For electrodes consisting of gold particles, the decrease in the characteristic size of the latter from 800 to 30 nm had virtually no effect on the current density (Fig. 16). However, further decrease in the size to 15–10 nm was accompanied by a substantial increase in the current density. It was concluded that the decrease in the particle size affects insignificantly the electrode catalytic properties up to the moment where the critical minimum size is reached. It is interesting that these conclusions agree with the results of studies [84–95] on the electrocatalytic properties of metal nanoparticles deposited on the nanotube surface.

IV. Adsorption properties of nanotubes

The remarkable features of nanotubes include their unique sorption characteristics. Insofar as carbon nanotubes are two-dimensional structures, their mass is localised in the graphene layer. This determines the abnormally high specific surface of nanotubes (the maximum theoretically possible value is ~1300 $m^2\ g^{-1}$ for one side of a graphene sheet) and is the reason for the peculiarities in their electrochemical and sorption properties. The real specific surface area is measured by the BET method.† For a sample that contains micropores, the latter are filled with liquid (condensed) nitrogen at pressures much lower than the saturated vapour pressure at a given temperature.[147] In the BET method, from the liquid nitrogen volume, the area occupied by the nitrogen monomolecular film is found, from which the effective (apparent) specific surface is determined. Thus, for different carbon materials that contain no nanotubes, the determined specific surface areas were at the level of

† This method provides correct results only for surfaces that contain no micropores.

3000 $m^2\ g^{-1}$. On the other hand, for SWNT, the external specific surface was found to be 500–700 $m^2\ g^{-1}$ for the cleanest samples of powder and nanopaper.

The adsorption of aniline and pyridine on carbon electrodes from organic and water–organic solvents was studied.[148] The electric double layer structure was found to be much different at the carbon electrode interfaces with ethanol, n-propanol, acetonitrile and water. Presumably, according to the De Levie model,[149] these differences are associated with the different conductivity of solvents, which causes irregularities in the resistance of electrolyte in the carbon matrix pores. A more detailed description of sorption properties of carbon nanostructures and also the information on different nanotube derivatives can be found in a review.[150]

Hollow single-walled nanotubes are conventionally used as the membranes and adsorbents.[151] Adsorption properties of nanotubes depend on three factors. The first factor is the number of adsorption sites. As was noted above, due to the strong van der Waals interaction, nanotubes are combined into bunches. However, it should be borne in mind that the space of bunches is not equally accessible for molecules and the sites of preferential location exist. Second, open ends of nanotubes can affect the adsorption capacity of a sample. It was found that closed nanotubes with the ends blocked by functional groups make a smaller contribution to the overall adsorption as compared with open nanotubes. Hence, to improve the sorption properties, nanotubes should be treated with the aim of opening their ends. Third, the insufficient purity of nanomaterial samples can limit the number of adsorption sites.

In a theoretical study[152] devoted to the adsorption of gas molecules in nanotube bundles, the adsorption kinetics was modelled by the Monte-Carlo method. It was assumed that the adsorption of particles in the form of one-dimensional chain can be described by two methods, namely, the external kinetics (considers the outer surface of nanotube bundles directly subjected to the gas action) and the pore-like kinetics (considers the gas diffusion through pores, inside tubes and between channels).

Effects associated with adsorption that are clearly manifested in autoelectronic emission at the nanostructured carbon–vacuum boundary were studied both theoretically[40–42] and experimentally.[43,44] From the viewpoint of electrochemistry, attention should be focused on the results of a study[40] that suggest that water molecules adsorbed on the nanotube vertices considerably enhance the tunnelling emission current. It was shown that in intense electric fields the binding energy increases at the tips of carbon structures as a result of which water molecules are stabilised there, which lowers their ionisation potential and favours the electron emission. The further decrease in the ionisation energy was associated with the formation of water clusters at the vertices of nanotube electrodes.

Similar conclusions were drawn[41] based on the assumption that the electron work function from nanotubes decreases in the presence of adsorbates. This favours an increase in the emission current (the increase is due to the adsorption-induced resonance states below the Fermi level). Hence, the parameters of the potential barrier for the electron escape should depend on the electron transfer between carbon atoms in nanotubes and the adsorbent atoms. Studying this effect[42] included analysing how the water molecules adsorbed on the nanotube vertices affect the ionisation potential. Presumably, due to electrostatic interactions between the dipole moments of aqua complexes built of one or several water molecules and a nanotube, the destabilisation of the higher occupied molecular orbital of the nanotube was observed as well as a decrease in the ionisation potential and an increase in the field emission. The ionisation potential of carbon nanotubes tended to decrease with an increase in the dipole moment of linear adsorbates.

An increase in the field emission current upon deposition of boron on the surface of carbon nanotubes was observed experimentally.[43] It was demonstrated that boron-covered nanotubes are characterised by a high local density of electronic states near the Fermi level. This was also confirmed by calculations, which demonstrated the lower electron work function from the nanotubes with boron atoms localised at their edges. The results of comprehensive studies of electron emission from open single-walled nanotubes with adsorbed anions BH^- and NH^- were published.[44] It was shown that the presence of adsorbates decreases the tunnelling barrier, intensifies the local field (especially at the ends of nanotubes), thus improving the emission characteristics.

Thus, in some cases, adsorbates can substantially promote the electron escape from nanotube cathodes. In connection with this, it is interesting to consider publications that discuss how the atoms adsorbed on the surfaces of carbon structures affect the electrochemical potentials of oxidation and reduction of depolarisers. Detailed studies of this phenomenon were carried out.[153,154] Particularly, it was considered[153] how the adsorption of phenothiazine dyes (Toluene Blue and Azure-C) affects the determination of dihydronicotinamide adenine dinucleotide (NADH) when carbon nanotubes are used as the electrodes. It was shown that the NADH oxidation current measured on an electrode with the adsorbed dye molecules on its surface was considerably higher than the current obtained on pure nanotubes. It should be noted that CV measured on the latter nanotubes containing no adsorption layers demonstrated no oxidation current of the studied compound in the concentration range under study. Moreover, in the presence of adsorbates on the surface of the studied electrode, NADH was oxidised at lower potentials.

Similar conclusions were drawn[154] based on the higher currents of guanine and adenine oxidation on a nanotube electrode in the presence of an adsorbate. This effect was explained by the electrostatic interaction of functional groups of adsorbates with the electrode surface, which favours the easier ET. The decrease in the overpotential and the increase in the CV peak height in hydrazine solutions was explained[155] by the presence of an adsorbed metallic impurity responsible for the electrocatalytic effect. Presumably, on such carbon structures, a lower detection limit can be reached in the analytical determination of hydrazine.

Adsorption of an electrochemically inactive organic adsorbate, camphor, on nanostructured carbon electrodes with different morphology (nanopaper, collumnar and filament structures) was studied.[156] The choice of this adsorbate was associated with the fact that camphor with its high attraction constant ($\geqslant 4.5$) forms a condensed adsorption layer on smooth metal electrodes and the parameters of this layer are well known (see Ref. 157). Measurements of the differential capacitance for the nanopaper and columnar

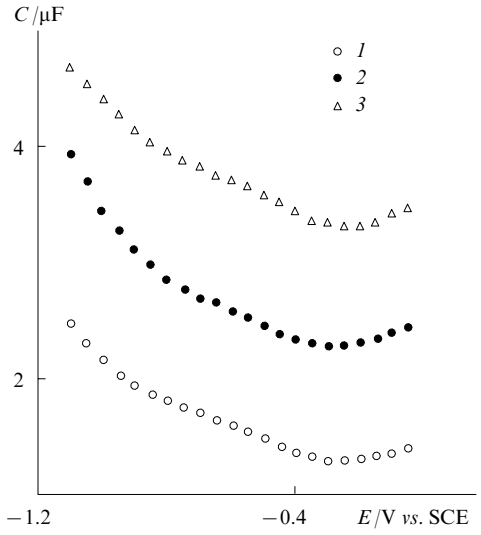


Figure 17. Dependences of the capacitance of a nanopaper electrode on the potential in 0.1 M Na_2SO_4 (*1*) and in the same solution containing 10^{-4} (*2*) and 10^{-3} mol litre^{-1} (*3*) of camphor.[156] Measuring frequency is 1117 Hz.

electrodes throughout the studied potential and frequency ranges have shown that, in sodium sulfate solutions containing 10^{-4} M camphor, the capacitance of these electrodes was 3–5 times higher than in solutions containing no adsorbate. Figure 17 shows the capacitance *vs.* potential dependence for a nanopaper structure.

The observed effect can be unambiguously associated with the increase in the real electrode capacitance, because the contribution of pseudocapacitance to the measured capacitance values can be neglected bearing in mind the absence of noticeable faradaic currents in the potential range from −0.7 to −0.1 V *vs.* SCE and the high measuring frequencies.

In the presence of a condensed adsorption layer, the electric double layer capacitance on the studied surface decreased. This experimental fact can only be explained by a substantial increase in the electrode surface accessible for the electrolyte. Bearing in mind the different morphology of nanopaper and columnar electrodes (*e.g.*, see Fig. 14), the increase in the differential capacitance was associated with the partial destruction of bunches that combine SWNT in the case of a nanopaper electrode and also of carbon 'flakes' that form oriented columnar structures. It is very likely that this is a sort of manifestation of the Rehbinder effect in electrochemistry.[158] In essence, this effect consists in the plasticising action of solutions of organic surfactants on solid materials. From the viewpoint of thermodynamics, the Rehbinder effect is caused by a decrease in the work of new surface formation upon deformation of a solid as a result of a decrease in its free surface energy under the effect of environment. The molecular mechanism of this effect manifests itself in facilitation of the rupture and restructuring of intermolecular (interatomic, interionic) bonds in a solid in the presence of certain adsorption-active and, at the same time, mobile foreign molecules (atoms, ions).[159] A similar effect was observed in the electrochemically initiated incorporation of alkali metal ions into the bundles of single-walled carbon nanotubes followed by partial destruction of bundles.[42] The presence of traces of a water-soluble surfactant on nanofibres could lead to an increase in the surface accessible to electrolyte as compared with the surface measured by the BET method.[112]

In contrast to nanopaper and columnar electrodes, the filament structures demonstrated an insignificant decrease in the capacitance, namely, 1.2–1.3-fold, in the same potential and frequency ranges. This also points to a certain increase in their capacitance associated with the increase in the accessible electrode surface, which prevails over its decrease due to the adsorption. The latter fact agrees with the electron spectroscopic data according to which the surface of carbon nanofibres is formed by soot-like structures that are probably incapable of severe loosing in the adsorption of organic substances (see Fig. 14 *b*).

V. Conclusion

The analysis of literature data has shown that electrodes containing nanostructured carbon of different morphology exhibit the electrocatalytic effect in the oxidation and reduction of different (both organic and inorganic) depolarisers. However, no generally accepted explanation for such a phenomenon is known. Some authors associate the electrocatalysis of electrodes with their large effective surfaces and the presence of functional groups and adsorbates on these surfaces. The other (including the authors of the present review) focus attention first of all on the topological surface defects with the atomic size and also on the features of the electronic structure of nanoforms. Hence, it is correct to conclude that the peculiarities of electrode reactions on atomically sharp areas of nanostructured carbon are caused by something else besides their large specific surface area. It other words, the use of carbon nanostructures as electrodes should change both their quantitative characteristics (due to the abnormally high specific surfaces) and qualitative properties (such as the overpotential of the depolariser electroreduction and electrooxidation or the potentials of redox reactions), which in fact means that the rate constant for the electron transfer depends on the electrode surface curvature. First of all, this follows from the decrease in the overpotential of different electrode reactions, which was observed in virtually all studies of nanostructured electrodes. Moreover, the sufficiently clearly traceable analogy with the field-emission characteristics of nanotubes that are also determined by the presence of high-curvature areas is beyond question.

This effect is of fundamental importance for the development of theoretical concepts of the electron transfer as an elementary act of any electrode reaction. At the same time, irrespective of the physical reasons for the easier ET on the electrode surface with high curvature, the surface modification by changing its morphology opens up wide prospects for exerting control over electrode processes. Undoubtedly, this method is of practical interest because the injection of electrons to solution from nanostructured electrodes of different nature allows one to 'bypass' the potential-controlling heterogeneous reaction of the first electron transfer.

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