

Chapter 10

Nanosensor Systems Simulations

We focus our research on two important directions of real-time control nanosystems addressed to ecological monitoring and medical applications, both of which provide environmental security for the human society and every individual. Ecological monitoring has been widely presented in [1]. For individual application, it is necessary to develop nanodevices with various functions for the human body, particularly for the control of health parameters, the enhancement of human abilities and prosthetics. Another course of development of nanosensors, nanoactuators, nanotransducers, etc. is the creation of artificial systems such as artificial intelligence or artificial individual [2, 3].

There are some successful schemes of nanosensors based on FET-type devices where induced conductivity changes in included nanocarbon elements (e.g. CNT or GNR) are indicators of external influence intensities. For chemical and biological agents, nanocarbon elements should be purposely functionalized [2].

We pay attention to the development of bio-nanosensors based on polymer nanoporous structures (nanotracks) with various enzymes, which provide the corresponding biocatalytic reactions and give reliably controlled ion currents [4, 5]. In particular, we describe a concept for a glucose biosensor based on the enzyme glucose oxidase (GOx) covalently linked to nanopores of etched nuclear track membranes. Using the simulation of chemical kinetics glucose oxidation with glucose oxidase, we have obtained theoretical calibration dependences, when the concentration of H^+ is proportional to the concentration of the detected glucose. Experimental and theoretical calibration dependences demonstrate similar trends. The proposed device can serve to detect physiologically relevant glucose concentrations. The catalytic sensor can be made reusable due to the production of diffusible products from the oxidative biomolecular recognition event. Moreover, we can develop a multi-agent packet nanosensor, which can be used for human breathing analyser in relation to cancer detection, hepatitis and so on.

We consider physical nanosensors (pressure and temperature) based on functionalized CNT and GNR nanostructures. The model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric

polymer environments (e.g. epoxy resins) is regarded as a disordered system of fragments of nanocarbon inclusions with different morphologies (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric environment. The electrical conductivity of a nanocomposite material depends on the concentration of nanocarbon inclusions (in fact, carbon macromolecules). The basic conductivity mechanism for the considered nanocomposites is the hopping conductivity. This mechanism can usually be observed, for example, in amorphous semiconductors or some disordered solids. Various nanocomposite morphologies are considered, and computer simulation results for pressure and temperature nanosensor models are discussed in comparison with the experimental nanodevice prototype.

The sensitivity of the considered nanosensors in this case depends on percolation ability of a nanocomposite subdued to the changes of physical factors (pressure or temperature). Attention should be paid to the nanoscaled quantum mechanical phenomenon of percolation ability among the neighbouring nanocarbon ‘islands’ within a nanocomposite. Integrated ‘micro’- or ‘mesoscale’ conductivity effects should also be evaluated as a goal for calibration of a nanocomposite material as a measurement tool for pressure or temperature [3–5].

10.1 Physical and Chemical Nanosensors

Nanosensor systems constitute an essential functional part of any modern device that provides information processing for information systems, engineering interfaces, healthcare and many others. The talk is about nanosensor systems for various aspects of ecological monitoring and security.

The fundamental electronic devices are nanocarbon-based FET transistors capable of providing high sensitivity to various external influences of different nature. In particular, changes of local electronic density of states correlate with corresponding physical, chemical and biochemical influences and lead to FET-device conductivity changes. Conventional schemes of nanosensing systems are based on nano-FET-type devices [1–5].

However, these types of nanosensors are oriented on local external influences at atomic or molecular levels, when the external agent has a direct contact with nanocarbon surface atoms, like in FET-type nanosensors (see Fig. 10.1).

10.1.1 Conductivity as a Tool of Nanosensor Systems

The calculations of conductivity are usually performed using Kubo–Greenwood formula [1, 2, 34]:

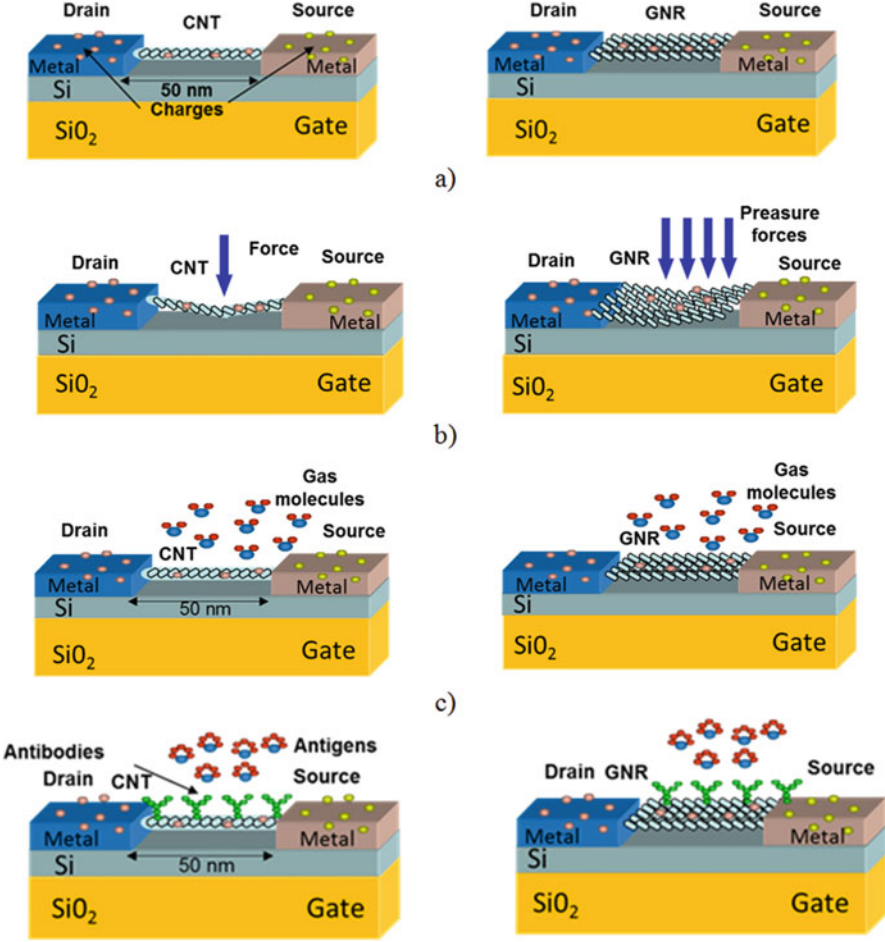


Fig. 10.1 Models of FET-type nanosensors as a prototypes of novel nanodevices: **(a)** the unperturbed field-effect transistors based on CNT or GNR elements; **(b)** physical nanosensors, a conducting threshold can be altered when the tube or graphene ribbon is bent; **(c)** chemical nanosensors, a conducting threshold can be altered when the amount of free charges on the tube of graphene ribbon surface is increased or decreased by the presence of donor or acceptor molecules of specific gases or composites, **(d)** biological nanosensors, monitoring of biomolecular processes such as antibody/antigen interactions, DNA interactions, enzymatic interactions or cellular communication processes, among others

$$\sigma_E(\omega) = \frac{\pi\Omega}{4\omega} \int [f(E) - f(E + \hbar\omega)] |D_E|^2 \rho(E) \rho(E + \hbar\omega) dE, \quad (10.1)$$

where ω is a real frequency parameter of Fourier transform for the time-dependent functions; $f(E)$ is Fermi–Dirac distribution function; $D_{E,E'} = \int_{\Omega} \Psi_{E'}^* \nabla \Psi_E d\mathbf{r}$, where

$\Psi_{E(\mathbf{K})} = A \exp(i\mathbf{K}\mathbf{r})$; and $\mathbf{K}$ is the complex wave vector of the effective medium. The dispersion function $E(\mathbf{K})$ determines the properties of the wave function $\Psi_{E(\mathbf{K})}$ upon the isoenergy surface in $\mathbf{K}$ -space.

Usually two basic electron conductivity mechanisms in CNT-based structures are considered. The ballistic mechanism is engaged in electron transport within CNTs, while the collisional mechanism is a characteristic of CNT–substrate interconnects. The general conductivity σ_{gen} is evaluated as follows: $\sigma_{\text{gen}}^{-1} = \sigma_{\text{coll}}^{-1} + \sigma_{\text{ball}}^{-1}$.

For pure CNTs, we clearly observe that $\sigma_{\text{ball}} \gg \sigma_{\text{coll}}$. But Kubo–Greenwood formalism is free from this division on ballistic and collisional mechanisms and seems to be more objective. The analysis of Kubo–Greenwood’s conditions in respect of CNT morphology has been presented taking into account both *dc* ($\omega = 0$) and *ac* ($\omega \neq 0$) regimes as well as the temperature factor of electron transport.

We use in this research the results of *ab initio* electronic structure calculations of D’yachkov et al. [6] based on the linear augmented cylindrical wave (LACW) theory of the perfect SWCNT band structure. The developed generalization of this method allows one to treat the electronic structure of various defects in the SWCNTs. The method combines the advantages of density functional *ab initio* theory with the Green’s function approach to the point defects electronic structure.

The main aim of our research is a simulation on sensitivity of SWCNTs to various defects which evidently change the local EDOS and then, as a result, give the changes of conductivity. The detailed properties of EDOS at the vicinity of Fermi level are essential for expected conductivity values.

Figure 10.2 shows the parametric simulations of *ac*-conductivity for *armchair* (m,m) CNTs, where the essential sensitivity to the radius of SWCNT for energies more than 0.5 eV is shown.

But, there is no essential dependence on chirality number m for THz-range, excluding $m = 4$. Figures 10.3 and 10.4 demonstrate the comparison of conductivity calculations for pure perfect and doped (B or N) CNTs (5,5) and (7,7) in the case of noninteracting defects.

Numerical simulations of conductivity have been carried out for *zigzag* ($m,0$), *armchair* (m,m) and *chiral* (m,n) CNTs, where the sensitivity of conductivity has been demonstrated to the local electronic density of states in CNTs with local impurities (N and B atoms). In particular, this sensitivity means that the potential possibility of CNT-based nanodevices is to be used as nanosensor systems. This means that the calibration of such nanosensors on current is possible.

Similar calculations for graphene-based structures on the basis of EDOS [9] (graphene, CO-graphene, Al-doped, Al-graphene and Al-CO-graphene) are shown in Fig. 10.5.

Doping technology of graphene is problematic [7]. However, taking into account that edges of GNRs can be considered as an extended topological defect, we pay attention to these regions as possible tools of nanosensing. Extended defects in

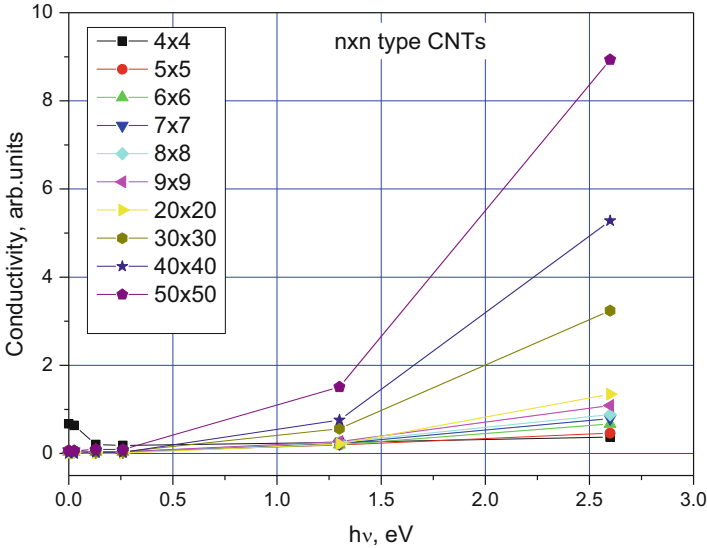


Fig. 10.2 Conductivities of perfect *armchair* SWCNTs of various morphologies. *Note:* the critical frequency of about 0.25 eV corresponds to 60 THz

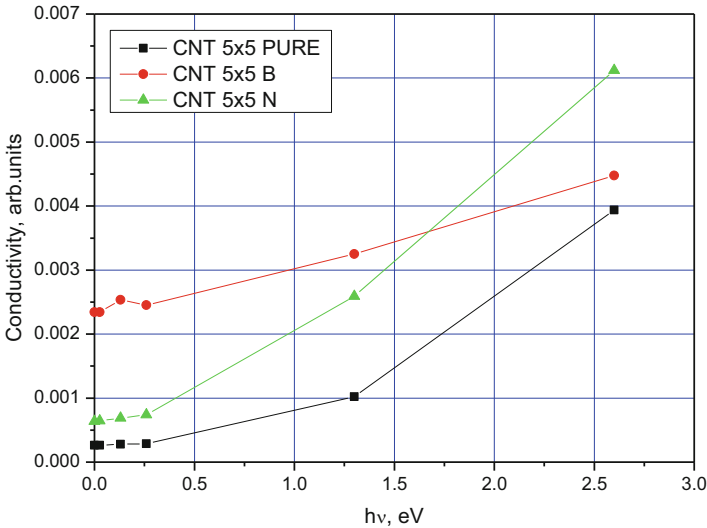


Fig. 10.3 Conductivities of pure perfect and doped (B or N) CNTs (5,5) in the limit of noninteracting defects

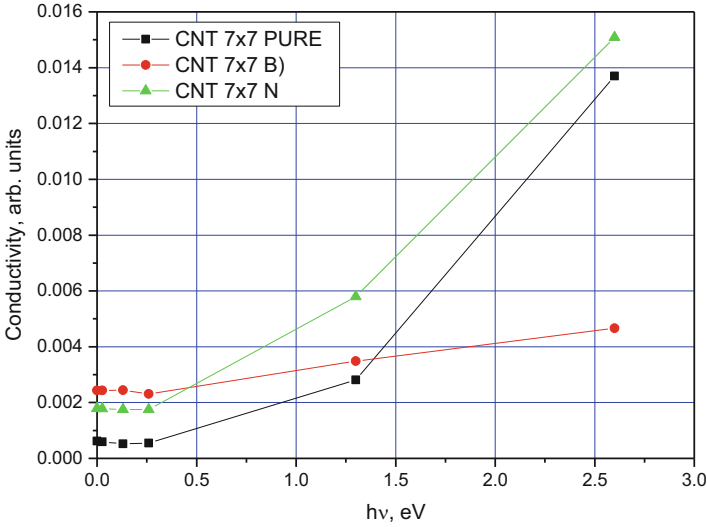


Fig. 10.4 Conductivities of pure perfect and doped (B or N) CNTs (7,7) in the limit of noninteracting defects

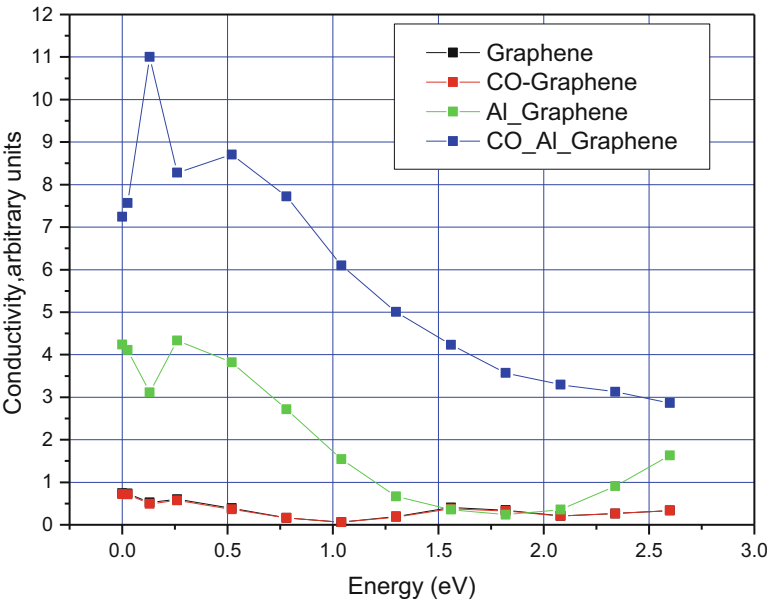


Fig. 10.5 Conductivities of pure perfect and Al-doped graphene for EDOS of [9]

graphene sheets, such as grain boundary (GB) defects, have been observed in some experimental investigations [8, 9]. Our calculations for pure and N- and B-doped GB on the basis of EDOS given in [10] are presented in Fig. 10.6.

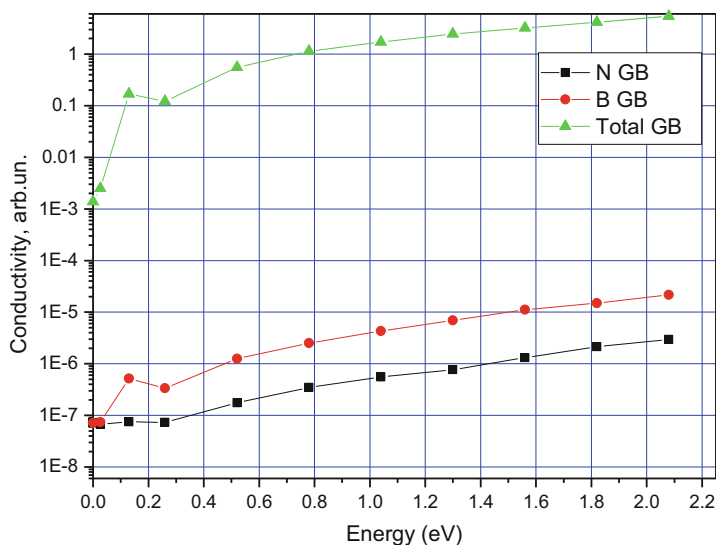


Fig. 10.6 Conductivities of pure and N- and B-doped GB on the basis of EDOS in [10]

10.2 Bio-nanosensors: *Polymer Nanoporous Model Structures*

Since the 1960s, it has been known that energetic (with tens of MeV or more) heavy (with atomic masses being usually larger than that of Ar) ion irradiation ('swift heavy ions', SHI) introduces very narrow ($\sim$ some nm) but long (typically 10–100 μm) parallel trails of damage in irradiated polymer foils, the so-called latent ion tracks. The damage shows up primarily by the formation of radiochemical reaction products. Whereas the smaller ones readily escape from the irradiated zone, thus leaving behind themselves nanoscopic voids, the larger ones tend to aggregate towards carbonaceous clusters. Thus, emerging structural disorder along the tracks modifies their electronic behaviour (see Fig. 10.7).

Description of the sensing reaction of glucose with the enzyme GOx looks as follows:

- The overall net reaction is glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) + O_2 (due to enzyme-induced oxidation) gluconic acid ($\text{C}_6\text{H}_{12}\text{O}_7$) + O .
- This remaining O attaches to some H_2O to form peroxide H_2O_2 .
- The product, gluconic acid, dissociates around $\text{pH} = 7$. Thus, the conductivity of the liquid changes (essentially if the product is enriched in the track's confinement); this is what is measured by the sensor [11, 35].

In particular, a complicated biochemical kinetics of basic reaction of glucose detection depends on track qualities (e.g. track creation mechanism, foil material properties), enzyme (GOx) distribution on the track surface, geometry of the etched

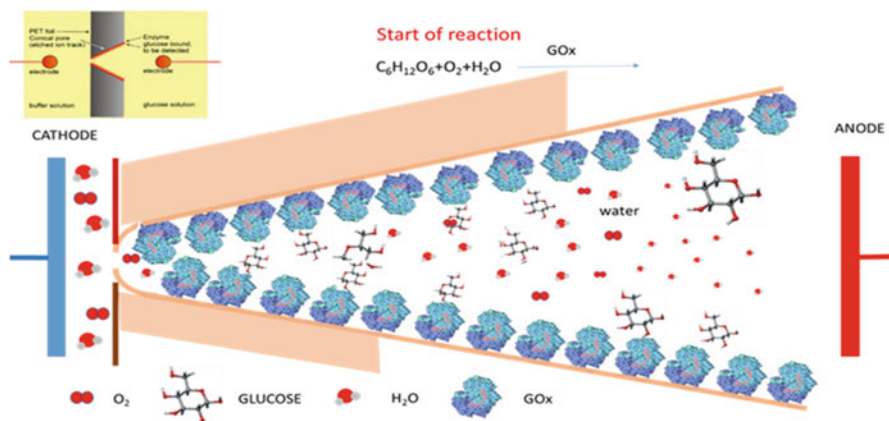


Fig. 10.7 General scheme describing the detection scheme and modified polymer. Principle arrangement of experimental setup to study current-voltage dependences in ion track-containing foils embedded in electrolytes

track, etc. All these factors are the subject for the nearest special research. Moreover, the detailed kinetics of reaction is the object of 3D-modelling to design the optimal geometry of nanosensor active space. This allows creating optimal nanosensors with the increased efficiency.

The newly created intrinsic free volume enables electrolytes to penetrate into the polymer, thus forming parallel liquid nanowires. In case of tracks penetration through all the foil, the conducting connections emerge between the front and back sides of the foil. The ion track technology is particularly intended to biosensing applications. In this case, the ion tracks are functionalized directly by attaching organic or bioactive compounds (such as enzymes) to their walls.

10.2.1 Biosensor Model Testing and Experimental Results

Experimental and theoretical calibration dependences demonstrate similar trends. The proposed device can serve to detect physiologically relevant glucose concentrations. The catalytic sensor can be made reusable due to the formation of diffusible products from the oxidative biomolecular recognition event. Moreover, we can develop a multi-agent packet nanosensor, suitable for application as a human breathing analyser in relation to cancer detection, hepatitis and so on [11–15].

The recent advancements in the field of nanosensor design allow monitoring and tracking biomolecules in such areas as the environment, food quality and healthcare. The presently developed ion track-based nanosensors provide high sensitivity, reliable calibration (see Fig. 10.8), small power and low cost.

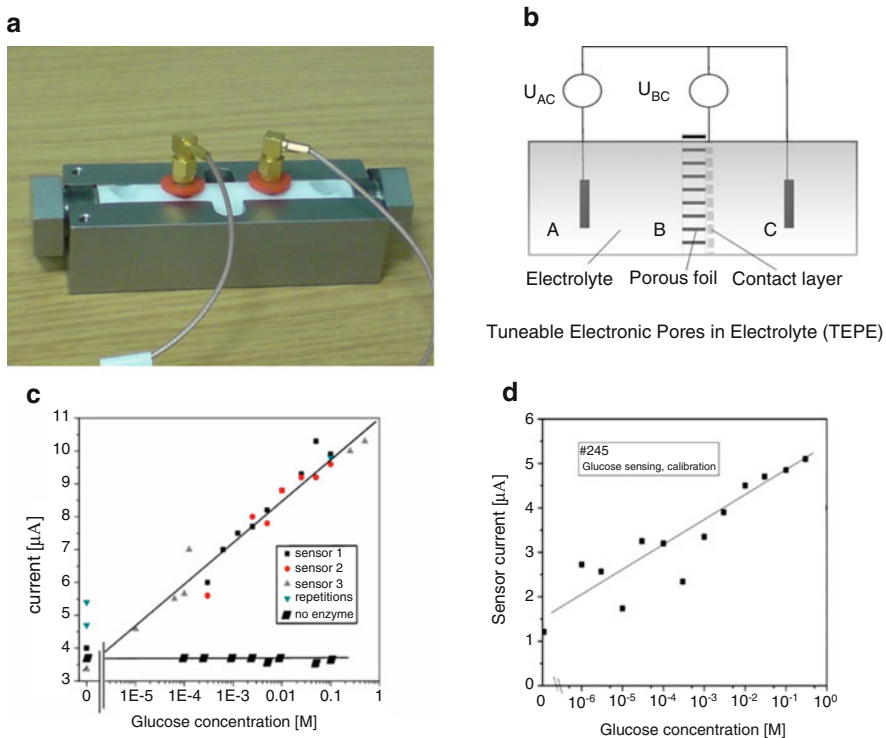


Fig. 10.8 Favourable platform for measuring enrichment of chemical reaction products via electrical current transmitted through the nanopores: (a) nanosensor system prototype [11]; (b) principal electrical scheme of sensor current [11]; (c) experimental calibration curves on 2007 year glucose testing series [11], experimental calibration dependence performance comparison of three identically produced track-based glucose detectors against a calibration curve I (+5 V) vs glucose concentration; (d) similar experimental calibration curve on 2016 year glucose testing series [16]

Using simulation of chemical kinetics glucose oxidation with glucose oxidase (see Fig. 10.9), we have obtained theoretical calibration dependences, when the concentration of H^+ is proportional to the concentration of the detected glucose.

Simulation schemes are directed on concentrations of H^+ which are equal to glucose concentrations. In cases of stable of glucose, inputs we obtain can write typical simulation equations which lead to the saturated values of H^+ ions concentrations (see Fig. 10.10):

$$\begin{cases} \frac{d}{dt}[C_6H_{12}O_6] = -w_1 \\ \frac{d}{dt}[H_2O_2] = w_1 - w_2 \\ \frac{d}{dt}[O_2] = -w_1 + w_2 \\ \frac{d}{dt}[H^+] = 2w_1 \end{cases} \quad (10.2)$$

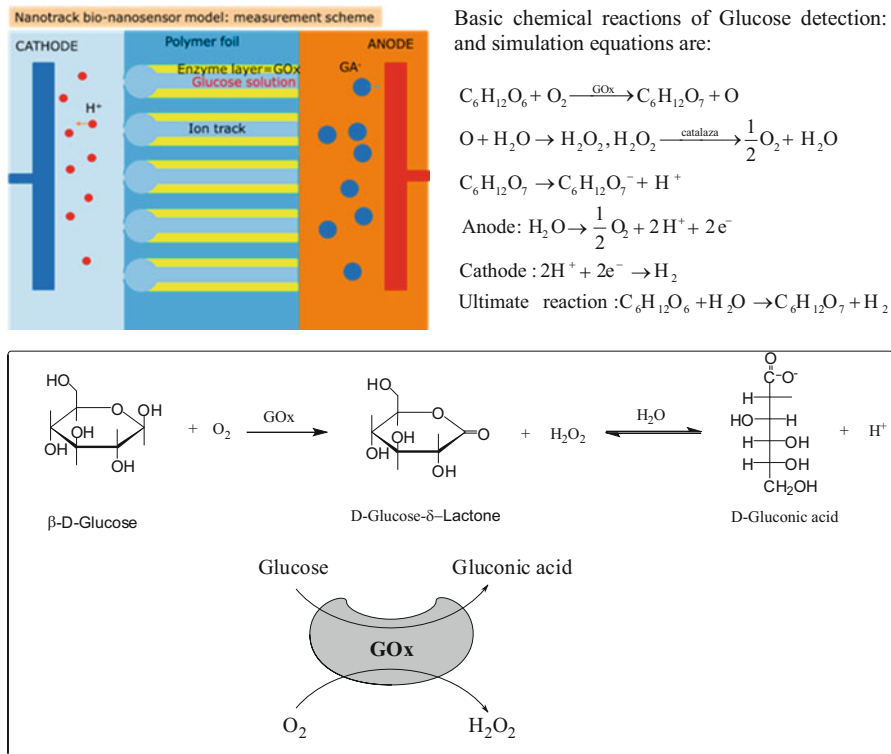


Fig. 10.9 General model of glucose detection process on the ion track-containing foils embedded in electrolyte and basic set of biochemical reaction [11, 12, 15]

where $w_1 = k_1[\text{C}_6\text{H}_{12}\text{O}_6][\text{O}_2][\text{GOx}]$ and $w_2 = k_2[\text{H}_2\text{O}_2]$ are the reactions rates and k_1 and k_2 are simulation parameters.

We can point out that theoretical simulation results demonstrate similar linear trend in comparison to experimental data (see Fig. 10.8c, d).

Taking into account the probable process of H⁺ ions recombination, we can modify simulation Eq. (10.3) as:

$$\begin{cases} \frac{d}{dt}[\text{C}_6\text{H}_{12}\text{O}_6] = -w_1 \\ \frac{d}{dt}[\text{H}_2\text{O}_2] = w_1 - w_2 \\ \frac{d}{dt}[\text{O}_2] = -w_1 + w_2 \\ \frac{d}{dt}[\text{H}^+] = 2w_2 - 2w_3 \end{cases} \quad (10.3)$$

where $w_1 = k_1[\text{C}_6\text{H}_{12}\text{O}_6][\text{O}_2][\text{GOx}]$, $w_2 = k_2[\text{H}_2\text{O}_2]$ and $w_3 = k_3[2\text{H}^+][2\text{e}^-]$ are the reactions rates and k_1 , k_2 and k_3 are again simulation parameters (Fig. 10.11).

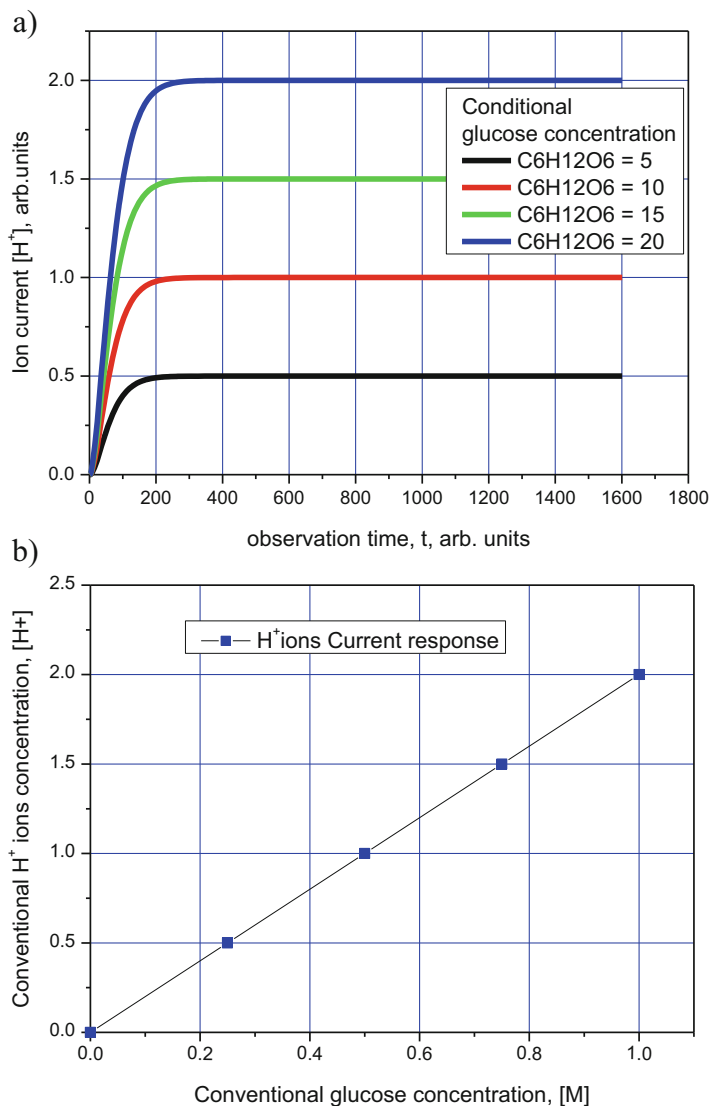


Fig. 10.10 (a) Simulation of H^+ ion current via observation time in case of saturation; (b) theoretical model of typical calibration dependence based on chemical kinetics results: simulation of induced H^+ ion current via glucose concentration

The creation of novel biosensors and their further improvement requires a careful study of the mechanisms of electrolytes passing through the tracks. Experimental and theoretical calibration dependences demonstrate similar trends. The proposed device can serve to detect physiologically relevant glucose concentrations. The catalytic sensor can be made reusable due to the formation of diffusible

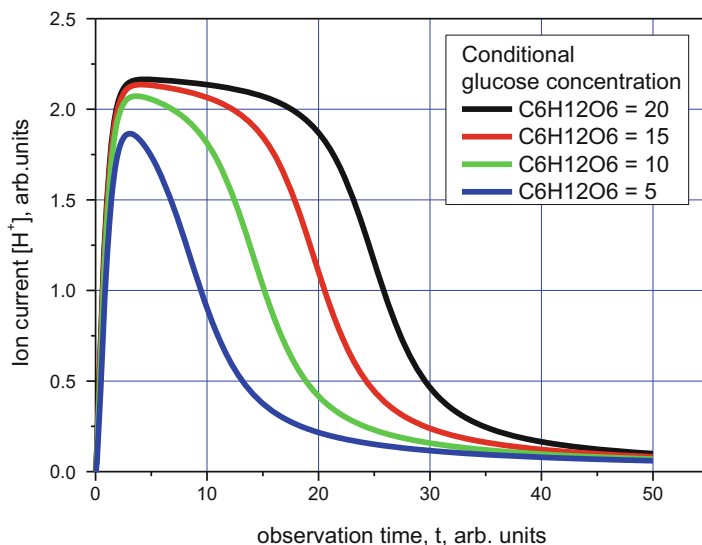


Fig. 10.11 Simulation of H^+ ion current via observation time in case of H^+ ions recombination

products from the oxidative biomolecular recognition event. Moreover, we can develop a multi-agent packet nanosensor, which can be used as a human breathing analyser in relation to cancer detection, hepatitis and so on (Fig. 10.12c).

Every nanocell (Fig. 10.12b) has an independent electrical metrology scheme. Moreover, sensitive cells for particular bioagent can be distributed along the sensitive surface of multi-agents flux. All electrical responses corresponding to a particular bioagent accumulated digitally as calibrated medical data on the special integrated screen.

10.3 Nanocomposite-Based Nanosensing Devices

10.3.1 Real-Time Polymer Nanocomposite-Based Physical Nanosensors

10.3.1.1 Methods and Models

We consider physical nanosensors (pressure and temperature) based on functionalized CNT and GNR nanostructures. The model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric polymer environments (e.g. epoxy resins) is regarded as a disordered system of fragments of nanocarbon inclusions with different morphologies (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric

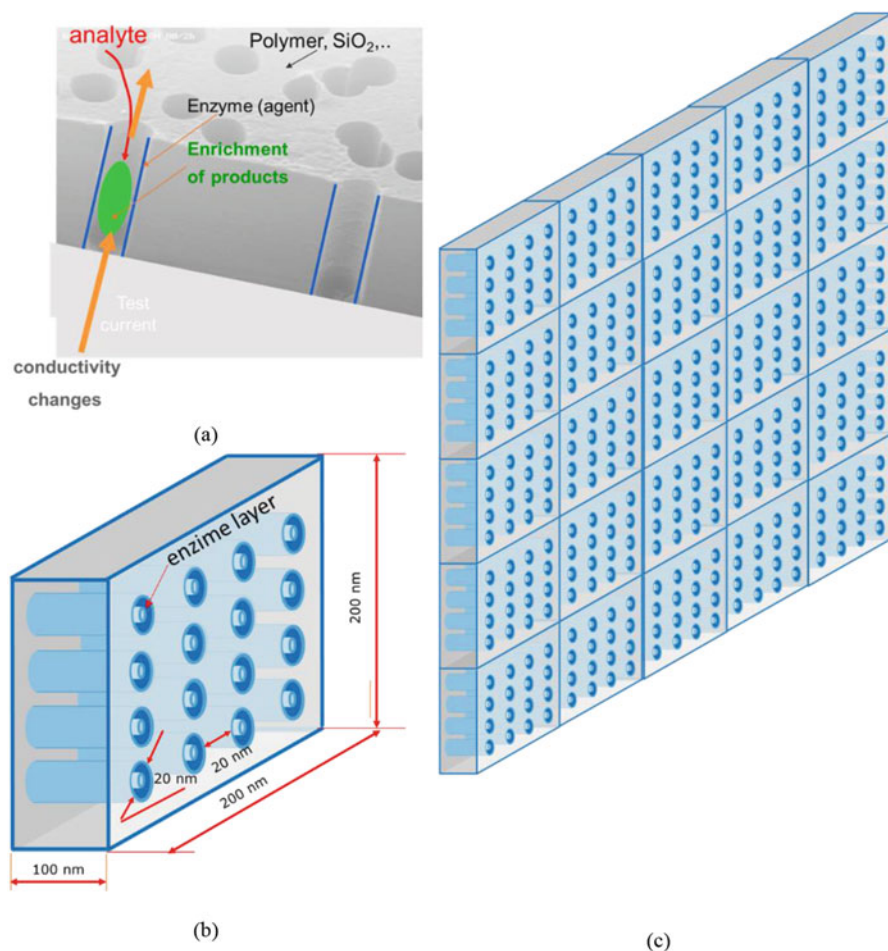


Fig. 10.12 Sensing of chemical reaction products of an analyte with a specific enzyme via the track conductivity: (a) nanotracks in the foil, (b) model of nanocell with nanotracks including to corresponding tested bioagent, (c) multi-agent testing nanocell matrix (5×5), where the matrix any cell element independently oriented on particular bioagent

environment. The electrical conductivity of a nanocomposite material depends on the concentration of nanocarbon inclusions (in fact, carbon macromolecules) and corresponding morphologies. We should evaluate the role of particular local conductivity mechanisms in nanocomposites using the cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as effective medium approximation (EMA-CPA) which we have effectively used for modelling of nanosized systems, especially for various nanointerconnect problems [17, 18]. We have found during conductivity calculations in CNT–metal and GNR–metal interconnects that the conductivity mechanism is very sensitive to local morphological disordering [19–21].

10.3.1.2 Conductivity Mechanisms

Considering models of physical nanosensors using CNT- and GNR-based nanocomposites, we should discuss conductivity mechanisms. In particular, in a medium with practically essential conductivity, it is useful to consider the phenomenon through the contributions of scattering effects that can take place in nanocomposite materials. We focus our attention on the four possible ways (see Fig. 10.13) trying to find the best description, in particular, for functionalized nanocomposites.

The key parameter for the analysis is the mean scattering length $\ell_{e-\text{gen}}$ of an electron in the conductive matter. In general, $\ell_{e-\text{gen}}$ includes various contributions in accordance with the well-known Matthiessen's rule, chapeau stating:

$$\frac{1}{\ell_{e-\text{gen}}} = \frac{1}{\ell_{e-e}} + \frac{1}{\ell_{e-a/\text{phon}}} + \frac{1}{\ell_{e-o/\text{phon}}} + \frac{1}{\ell_{e-o/\text{phot}}} + \frac{1}{\ell_{e-\text{impurity}}} + \frac{1}{\ell_{e-\text{defect}}} + \frac{1}{\ell_{e-\text{boundary}}} + \dots, \quad (10.4)$$

where ℓ_{e-e} is the electron–electron scattering length; $\ell_{e-a/\text{phon}}$ is the acoustic phonon (emission and absorption) scattering length; $\ell_{e-o/\text{phon}}$ is the optical phonon emission scattering length, is the optical phonon absorption scattering length and is the electron–impurity scattering length; $\ell_{e-o/\text{phot}}$ is the electron–defect scattering length; and $\ell_{e-\text{impurity}}$ is the electron scattering length with the boundary.

Hydrodynamical character of electric conductivity is the fundamental property of certain metals at low temperatures [22, 23]. This quality can be observed for such cases, when the length of electron mean free path is the order of the sample character size, namely, $\ell_{e-\text{boundary}} \propto L$ and $\ell_{e-e} \ll L$.

The last relation should be precise in cases of collisional and non-collisional electronic plasma with concentrations less than 10^{17} cm^{-3} . Hydrodynamical behaviour of electron liquid is possible to observe in some critical spaces of metal-like graphene-based electronic devices [24].

Collisional mechanism is a more expanded conductivity mechanism and takes place in most cases of typical normal conditions, e.g. for metals and semiconductors. In this case $\ell_{e-\text{phon}} \propto a \ll L$, where a is the character distance between ‘scatterers’ – atoms. This mechanism for DC conductivity is described by the classical Drude model [25, 26]: $\sigma = \frac{ne^2\tau_{e-\text{phon}}}{m^*}$, where n is the electron concentration, e is the electron charge, $\tau_{e-\text{phon}}$ is the time electron–phonon scattering and m^* is the effective mass of electron.

Ballistic character of conductivity is characterized by transport of electrons in a medium having negligible electrical resistivity caused by scattering. Moreover, the scattering character is essentially elastic, and the medium should be considered ideally regular. The time of electro–phonon interaction is negligible. This mechanism is observed, for example, in GNRs and CNTs included in FET-type devices. The most popular description of ballistic mechanism was given by Rolf Landauer and is known now as Landauer–Büttiker formalism [27]. Landauer formula

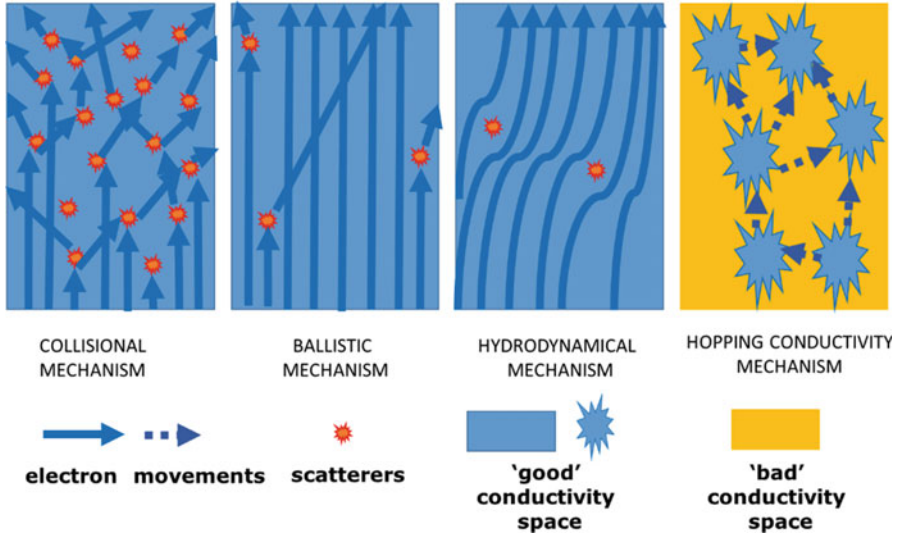


Fig. 10.13 Review of general mechanisms of electron DC conductivity

$G(\mu) = G_0 \sum_n T_n(\mu)$, where G is the electrical conductance, $G_0 = e^2/(\pi\hbar) \approx 7.75 \cdot 10^{-5}$ Ohm is the conductance quantum, $T_n(\mu)$ is the transmission eigenvalues of the channels and the sum runs over all transport channels in the conductor. The conductance can be calculated as the sum of all the transmission possibilities that an electron has when propagating with an energy E equal to the chemical potential μ . In fact, the phenomenon is similar to optical thin films effect, when the transparency is achieved due to the quantization of the wave length. However, it is impossible to realize the remarkable conductivity property of GNRs and CNTs without any contacts. Appropriate nanocarbon–metal interconnects are characterized as disordered regions with essentially scattering mechanism of conductivity.

Hopping conductivity mechanism was proposed for disordered condensed systems (e.g. for composite amorphous semiconductors and dielectrics) for the explanation of the metal–insulator transition [28]. The talk is about the existence of the electron hopping between the conductive clusters in the dielectric or between the impurity centres of localization. In this model, the medium (insulator–metal) is represented by the following pattern: there is a random distribution of the nodal points related to each other by ‘conductivities’ exponentially dependent on the interstitial distances. The hopping conductivity model with a variable ‘jump’ length can be considered the most general one $\ell_{e-\text{impurity}} \propto a$:

$$\sigma = A \exp\left(-\frac{4}{3} \left(\frac{4ar_s}{a}\right)^{3/4} \left(\frac{W}{\kappa T}\right)^{1/4}\right), \quad (10.5)$$

where a is the characteristic *borous radius* of the considered ‘doping’ centre, r_s is the characteristic radius of the doping centre or conductive region, W is the characteristic potential barrier for electron tunnelling, k is the Boltzmann constant, T is the sample temperature, $\alpha \approx 0.70$ is the empirical constant which can be evaluated only using Monte-Carlo numerical simulations [29] and σ_0 is the pre-exponential factor that is calculated taking into account the character of localization centre distribution.

10.3.2 Models of CNT- and GNR-Based Nanocomposites

We develop a set of prospective models of nanocarbon-based nanomaterials and nanodevices having various interconnects and interfaces. In particular, nanoporous and nanocomposite systems are considered as complicated ensembles of basic nanocarbon interconnected elements (e.g. CNTs or GNRs with possible defects and dangling boundary bonds) within the effective media type environment. Interconnects are essentially local quantum objects and are evaluated in the framework of the developed cluster approach based on the multiple scattering theory formalism as well as effective medium approximation [3, 4, 30].

In cases when nanocarbon clusters are embedded in high resistance media (instead of vacuum), we come to a nanocomposite material. The utilization of polymeric composite materials (e.g. epoxy resins) supplemented with various morphological nanocarbon groups of carbon nanotube type (CNTs) and graphene nanoribbons (GNRs) allows us to create effective pressure and temperature sensors. Application of such nanocomposites as coatings can provide continuous monitoring of the mechanical strains in piping systems (e.g. in aircraft or automotive applications), when the critical pressure values can indicate malfunctions of the engine. The analysis of possible medical instruments for real-time measuring human body temperature and blood pressure can also be realized.

The interest in CNT- and GNR-based polymer nanocomposites as prospective pressure and temperature nanosensor materials is based on the observed electric percolation phenomena via the nanocarbon inclusions concentration. In particular, the electrical conductivity of a nanocomposite increases with the increasing CNT loading up to a critical filler concentration, where a dramatic increase in conductivity is observed. This critical filler concentration is called electrical percolation threshold concentration. At percolation threshold concentration, a filler forms a three-dimensional conductive network within the matrix; hence electron can tunnel from one filler to another, and, in doing so, it overcomes the high resistance offered by insulating polymer matrix.

Consider the model of composite material with carbon nanocluster inclusions of CNT and GNR types (see Fig. 10.14).

The host material is a flexible dielectric medium of epoxy resin type with high resistance [5]. However, a low concentration of nanocarbon inclusions cannot change the mechanical properties of the host material. At the same time, high

Fig. 10.14 Model of composite polymer material with carbon nanocluster inclusions of GNR and CNT types

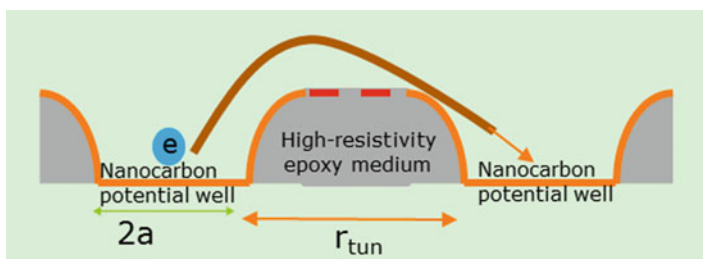
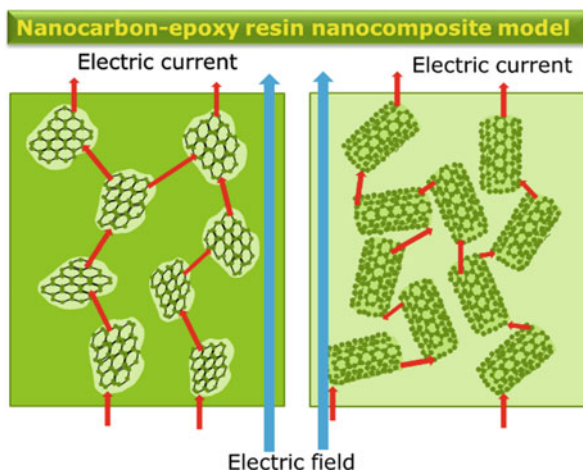


Fig. 10.15 Potential wells model for hopping in polymer nanocomposites, where $2a$ is the characteristic size of nanocarbon inclusion and r_{tun} is the length of the tunnel 'jump' of the electron

electrical conductivity of CNTs and GNRs incorporated in the host material can significantly affect the total conductivity of the nanocomposite material. According to our model, the mechanism of these changes is related to the effects of percolation through the hopping conductivity (see Fig. 10.15). This is the only mechanism that takes into account the compliance with our analysis-induced morphological changes in the whole nanocomposite matrix. This is a single mechanism which takes into account accordance with our analysis-induced morphological changes in the whole nanocomposite matrix.

Thus, the model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric polymer environments (e.g. epoxy resins) is considered as a disordered system of fragments of nanocarbon inclusions with different morphology (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric environment. Presumably, the electrical conductivity of a nanocomposite material will depend on the concentration of nanocarbon inclusions (in fact, carbon macromolecules). Isolated nanocarbon inclusions will provide conductivity due to the hopping conductivity mechanism

through dangling bonds up to the percolation threshold, when at high concentrations (some mass %) a sustainable ballistic regime appears, which is characteristic of pure carbon systems. The hopping mechanism is regulated by the electron hopping between ‘nanocarbon macromolecules’ (see Eq. (10.2) and [3, 28, 30]:

$$\sigma = A\sigma_0 \exp\left(-\frac{4}{3}\left(\frac{4ar_{\text{tun}}}{a}\right)^{3/4}\left(\frac{W_0}{\kappa T}\right)^{1/4}\right), \quad (10.6)$$

where r_{tun} is the length of the tunnel ‘jump’ of the electron equal to the distance between ‘nanocarbon’ clusters and σ_0 is the pre-exponential normalization factor, which means the conductivity of monolithic dielectric medium. This factor can be evaluated following the relationship: $\sigma_0 = \frac{16e^2 r_{\text{tun}}^3 N}{\pi \hbar a_0}$, where N is the concentration of localization centres, in our case, nanocarbon inclusions concentration. For arbitrary distribution of localization centres, $r_{\text{tun}}^3 N = 0.24$ [33].

Added to this is the effect of intrinsic nanocarbon cluster conductivity, which is dependent on its morphology. The electric conductivity will also depend on the spatial orientation of nanocarbon inclusions. It will be greater for the longitudinal electric field orientations and lower for the transverse ones. Of course, any spatial orientations are technologically possible. If we introduce the volume part as an indicator of the nanocarbon inclusions concentration, $\eta = \left(\frac{R_0}{R_0 + r_{\text{tun}}}\right)^3$, where R_0 is the average nanocarbon macromolecule radius and r_{tun} is the statistically averaged width of the potential barrier between the nearest nanoclusters, which is responsible for the percolation ability of the model nanocomposite. We should also diminish the hopping phenomena and percolation probability taking into account the nanocarbon macromolecule orientation within a hypothetical sphere embedded into high resistance dielectric medium. Based on this definition, we can obtain a contribution of potential nanocarbon clusters to nanocomposite conductivity as follows (see also Fig. 10.16):

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -\frac{4}{3}\left(\frac{4\alpha}{3}R_0\left(\eta^{-1/3} - 1\right)\right)^{3/4}\left(\frac{W_0}{\kappa T}\right)^{1/4}. \quad (10.7)$$

The overall conductance of nanocomposite material is evaluated using equivalent electric scheme (see Fig. 10.17 and [5]):

$$\Sigma \approx \Sigma_D + \Sigma_{NC}, \quad \Sigma_{NC} = \sum_{i=1}^N (R_i)^{-1},$$

$$R_i = A \sum_{k=1}^{N_i} \left(\sigma_{\text{nano},ik}^{-1} + \sum_{k=0}^{N_i} (N_{\text{eff},ik} \sigma_{\text{jump},ik})^{-1} \right), \quad (10.8)$$

where N is the number of conductivity channels, N_i is the number of nanocarbon clusters in the conductivity channel, N_{eff} is the number of effective tunnelling bonds

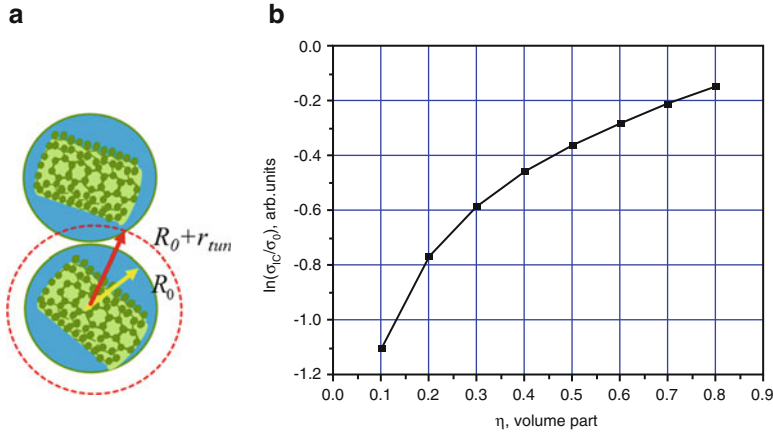
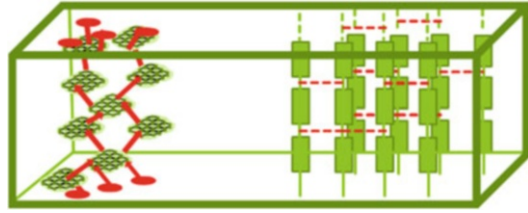


Fig. 10.16 Typical statistically averaged morphology of CNT–polymer nanocomposite: (a) structural model and (b) the hopping conductivity correlation via the average nanocarbon macro-molecules volume part within continuous dielectric medium

Fig. 10.17 Principle equivalent scheme of nanocomposite model for resistance calculation



including the contact region, $\Sigma_D = (R_D)^{-1}$ is the conductance of dielectric medium, σ_{nano} is the conductivity nanocluster and σ_{jump} is the hopping conductivity of the effective bond, which creates interconnect for large nanocarbon inclusion concentrations.

Basic nanocomposite models for simulation are presented in Fig. 10.18.

10.3.3 Simulation of Stress- and Temperature-Induced Resistance of Carbon-Based Nanocomposite Sensors: Results and Discussions

The basic dimensions of nanocarbon clusters (CNTs and GNRs) are as follows: the diameter of the CNT, 5 nm; the height, 10 nm, and the width of the expanded CNT, i.e. the width of the GNR $= \pi \cdot 5 \approx 15,6$ nm. The total height of model sensor is accepted as 100 nm.

The average statistical distance between nanocarbon clusters is 5 nm. This is the key distance for the mechanism of hopping conductivity. Nanocarbon cluster is

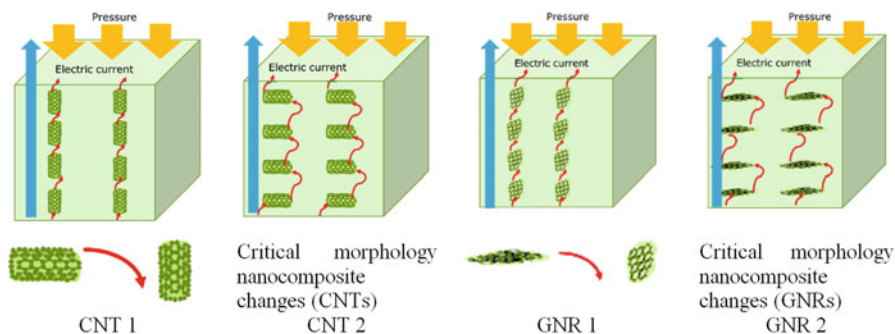


Fig. 10.18 Models of nanocarbon-based functionalized polymer nanocomposites: CNT configuration 1, CNT configuration 2, GNR configuration 1, GNR configuration 2, — electric field direction

considered as a potential well with a typical size $2a$. Neighbouring potential wells are separated by a distance r_{tun} . These two parameters ultimately determine the morphology of the nanocomposite material. For modelling it is also necessary to recalculate a microscopical parameter of relative jumping length to macroscopic strain parameter $\varepsilon = \Delta L/L$ in Hooke's law $\sigma = E\varepsilon$, where L is the total sample length. In cases of longitudinal orientation of CNTs (configuration CNT 1), the recalculation looks as:

$$\varepsilon = \frac{\Delta L}{L} \approx \frac{\Delta r}{r} \cdot \frac{1}{1 + \frac{1}{1+(1/n)} \cdot \frac{l}{r}},$$

where l is the CNT length (close to $2a$) and n is the number of CNT inclusions along the line (current direction). For transversal CNT orientations (configuration CNT 2), the similar recalculation looks as:

$$\varepsilon = \frac{\Delta L}{L} \approx \frac{\Delta r}{r} \cdot \frac{1}{1 + \frac{1}{1+(1/n)} \cdot \frac{d}{r}},$$

where d is the diameter of the CNT. The proposed model of hopping conductivity for current percolation in carbon-based epoxy resin nanocomposite takes into account basically the percolations along the nanocluster sets which are located along the stress direction. Interactions between the neighbouring sets are not considered for a low general concentration of nanocarbon inclusions.

In cases of longitudinal orientation of GNRs (configuration GNR 1), the recalculation looks as:

$$\varepsilon = \frac{\Delta L}{L} \approx \frac{\Delta r}{r} \cdot \frac{1}{1 + \frac{1}{1+(1/n)} \cdot \frac{h}{r}},$$

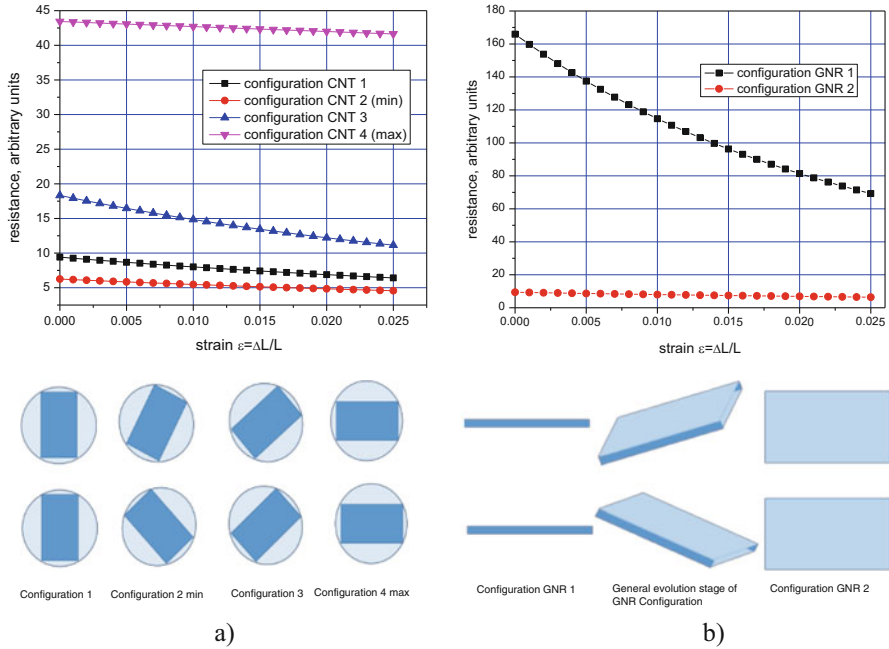


Fig. 10.19 Simulation of nanocarbon composites resistances via strain: (a) CNT configurations and (b) GNR configurations

where h is the GNR height (close to $2a$) and n is the number of GNR inclusions along the line (current direction).

For transversal GNR s orientations (configuration GNR 2), the similar recalculation looks as:

$$\epsilon = \frac{\Delta L}{L} \approx \frac{\Delta r}{r},$$

where d is the diameter of the GNR.

Figure 10.19 demonstrates resistance correlations via static stresses for ideal morphologies of a nanocomposite when CNTs and GNRs are oriented pure longitudinally, pure transversely. Configurations CNT 2(min) and CNT 4(max) correspond to the minimal and maximal tunnelling (jumping) distances due to the angle deviation of CNTs relatively longitudinal orientation.

From the technological point of view, it is not so simple to provide such ideal orientations for host polymer materials similar to epoxy resins. The first problem of the nanocomposite morphology is the selection of CNTs and GNRs with identical parameters. The second problem is the polymer–nanocarbon mixture creation when we evidently should expect a homogenous random distribution of nanocarbon orientations. Figure 10.20 demonstrates the marginal rotational disordering of CNTs inclusions from ‘ideal’ longitudinal orientation. Deviations of orientations

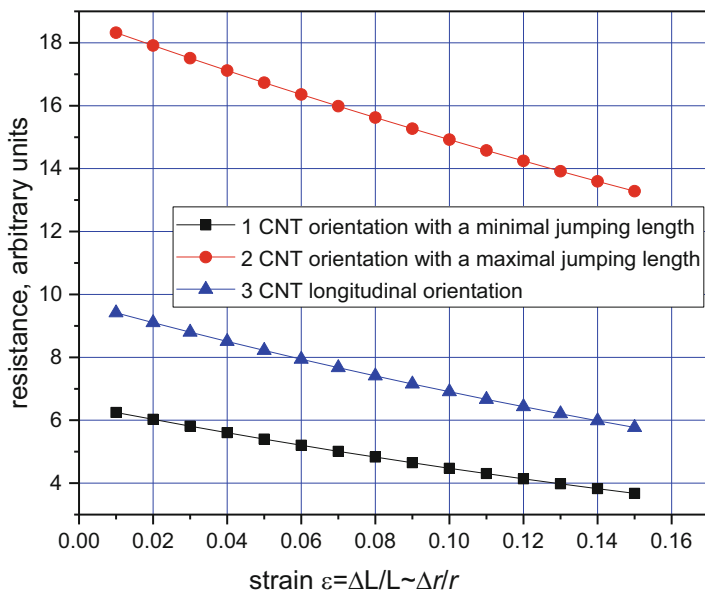


Fig. 10.20 Simulation of nanocarbon composites resistances via strain for rotational deviations of CNT inclusions

give the characteristic intercluster distances of 3.82 nm (see Fig. 10.19a, Configurations 2,3) and 7.02 nm (see Fig. 10.19a, Configurations 4) taking into account basic 5 nm in the ideal case.

Figures 10.19 and 10.20 present the full-scale simulation of CNT orientation deviations within a host material. The results show various sensitivity of the model nanocomposite as a potential pressure nanosensor in dependence of its morphology. Configurations of the fourth type (see Fig. 10.18) are more sensitive and, evidently, more practically preferable.

The model uses morphologically compatible carbon nanoconfigurations with the same number of carbon atoms, the same surface area of model CNTs and GNRs, and the same chirality. In this way, the model CNTs and GNRs are interconnected by a simple topological transformation from a cylinder to a rectangular fragment.

10.3.3.1 Modelling and Experimental Results

In this section, we will discuss the correlation of simulation results for pressure and temperature nanosensors with the experimental data of the particular prototype of similar devices [30, 36], where the developed technology of functionalized nanocomposite based on epoxy resin (*ED-20, GOST 10587–84. epoxy-diane resins uncured, elasticity modulus $E = 3.05$ GPa, mass density $\rho_m = 1.16–1.25$ g/cm³*) with multiwalled CNT inclusions was applied. The testing of the mentioned

nanosensors with various CNTs morphologies and mass concentrations (1%, 2%, 3%) was carried out for temperatures ranging from 27 till 90 °C and the pressure ranging from 1 till 30 Bars. The pressure test was carried out on a machine Instron 5942.

When testing the pressure sensor, the load ranged from 0 to 500 N, which corresponds to the change in pressure from 0 to 30 Bars. The temperature test was carried out using a Brookfield TC-502 water bath. The sensor sample was protected with a waterproof bag and placed in a water bath. The typical dependence of the sensor resistance on the pressure changes, as compared with the simulation results, is shown in Fig. 10.21a. Small deviations are connected with technological problems in the reproduction of perfect morphology, which reduces the percolation limit of the nanocomposite.

The typical dependence of the temperature sensor in the temperature range of 27–90 °C compared with the simulation results is shown in Fig. 10.21b. The discrepancy in behaviour between the experimental and theoretical dependencies is associated with morphological imperfections of the real sensor induced the orientation dispersion of CNTs. This effect can diminish the hopping mechanism efficiency, especially, for the higher temperatures.

Modelling of resistivity dependence via weight fraction of CNTs is presented in Fig. 10.22, where the sharp changes of resistivity within the weight fraction interval (0.08–0.12) are observed.

Evidently, this phenomenon can be explained by the increase in the percolation processes under the growing CNT weight fraction.

10.4 Concluding Remarks

Simulation of sensitivities of CNTs and GNRs to doping in FET-type devices demonstrates the efficiency of functionalization of nanocarbon elements in the process of creation FET-based nanosensors.

Our work has demonstrated that ion track-based glucose sensors can be effectively created. Furthermore, they show good sensitivity, they cover a wide range of medical applications, and they can be re-used at least ten times. This study also proves that track-based biosensors with other enzymes can be similarly developed.

The prototypes of nanocomposite pressure and temperature nanosensors have been simulated. The hopping conductivity mechanism gives the adequate description of possible nanosensor qualities. An important problem in manufacturing sensors based on CNTs and GRNs is nanocarbon inclusions orientation, which determines the electrical properties of the future nanosensors. Various nanocomposite morphologies are considered, and computer simulation results for pressure and temperature nanosensor models are presented in comparison with the experimental nanodevice prototype. A good correlation between the proposed

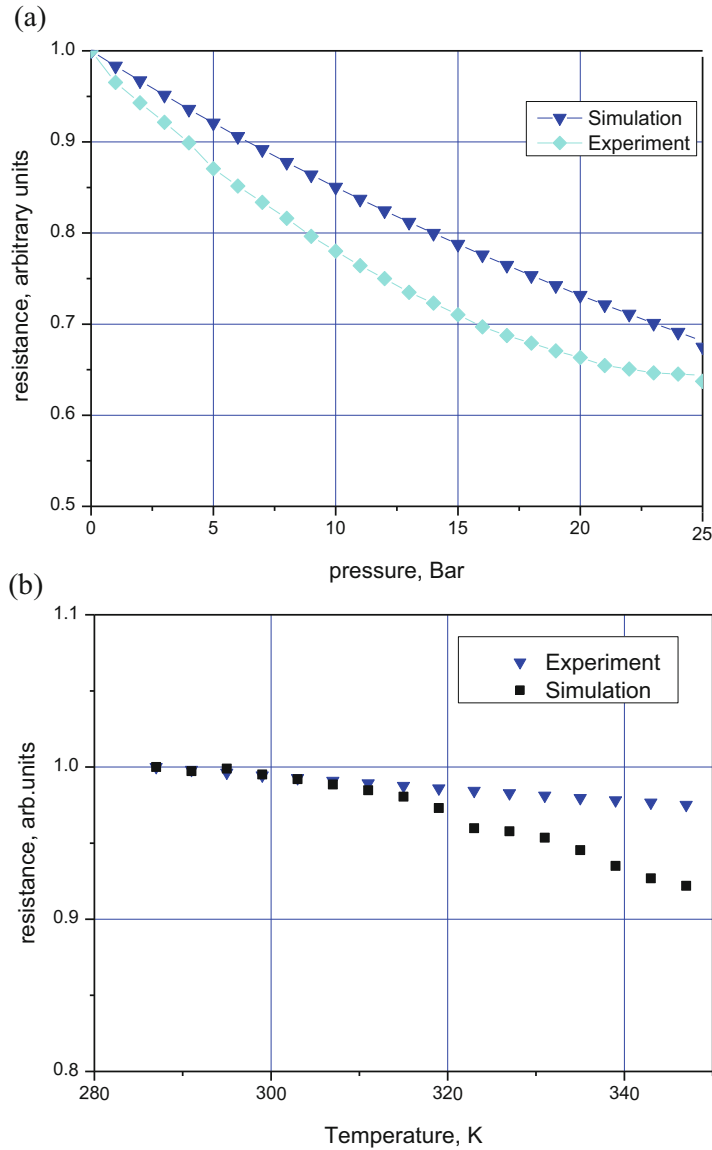


Fig. 10.21 Comparison of real pressure and temperature nanosensor indications [31] with more adequate models morphologies simulation: (a) pressure nanosensor and (b) temperature nanosensor

nanocomposite-based sensor model and the experimental one was shown. The developed mathematical model can be applied to polymer nanocomposites with inclusions of different types. Various morphologies of resistive network models can be realized for evaluation of the total resistance in different nanosensor prototypes.

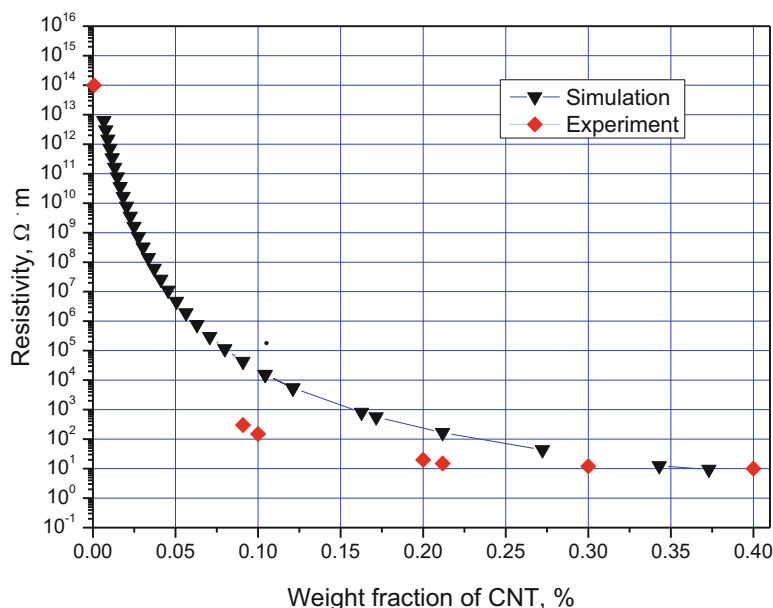


Fig. 10.22 Comparison of resistivity of developed model CNT-based nanocomposite via weight fraction of CNT with the experimental data [32]

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