Modelling and simulation of electric response of nanocarbon nanocomposites and nanoporous polymer based structures for nanosensor devices

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Abstract

The main objective of the current study is to demonstrate the implementation of advanced simulation models providing a proper description of electric responses in nanosensoring systems. Firstly, 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). Various nanocomposite morphologies are considered and computer simulation results are discussed. Secondly, we pay attention to development of bionanosensors based on polymer nanoporous structures (nanotracks) with various enzymes, which provide corresponding biocatalytic reactions and give reliably controlled ion currents. In particular, we describe a concept for a glucose biosensor based on the enzyme glucose oxidase covalently linked to nanopores of etched nuclear track membranes. This device can be used to detect physiologically relevant glucose concentrations. The sensitive catalytic sensor can be made re-usable due to the production of diffusible products fromt he oxidative biomolecular recognition event.

Keywords: carbon-based nanocomposites, epoxy resins, pressure and temperature nanosensors, hopping conductivity, track electronics, bionanosensors

1 Introduction

Nanosensor systems are essential functional parts of any modern devices of information processing for information systems, engineering interfaces, health etc. We can talk about nanosensor systems for various aspects of ecological monitoring and security. The fundamental electron devices are FET-transistors, which are able to provide high sensitivity to various external influences of different nature. Usual schemes of nanosensoring systems are based on nano-FET-types devices, namely:

a) the unperturbed field-effect transistors based on CNT- or GNR- based FETs are mainly composed of the corresponding semiconducting carbon materials suspended over two electrodes;
b) physical nanosensors: a conducting threshold can be altered when the tube or graphene ribbon is bent;
c) chemical nanosensors: the same 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, etc. [1, 2].

The other way of nanosensoring is the using of polymer nanoporous structures. In particular, ion tracks are suitable in biosensing applications because they have true nanometric dimensions. Ion tracks can confine chemical reactions in well-defined, pre-determined locations ensuring that their reaction products are highly enriched locally. If membranes containing such etched tracks are put in the path of ion currents flowing through a vessel, all the ions are subsequently forced to pass through the nanopores, electrically sensing any confined chemical reaction occurring there via changes in the pore's electrical resistance.

2 Nanocarbon nanocomposites based pressure and temperature nanosensors

We develop a set of prospective models of nanocarbon-based nanomaterials and nanodevices based on the 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].

In cases when nanocarbon clusters are embedded in high resistance media (instead of vacuum) we come to 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 (for example, in aircraft or automotive applications), when the critical pressure values can indicate malfunctions of the engine.

The interest in the CNTs and GNRs based polymer nano-composites as prospective pressure and temperature nano-sensor 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 till 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 CNTs- and GNRs- types. The host material – is a flexible dielectric medium of epoxy resin-type with high resistance. However, low concentration of nanocarbon inclusions cannot change the mechanical properties of the host material. At the same time, high 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. The hopping mechanism is regulated by the hopping of electron between 'nanocarbon macromolecules' (see also Figure 1):

$$\sigma_{IC} = \sigma_0 \cdot \exp\left(-\frac{4}{3}\left(\frac{4\alpha r_{IC}}{a}\right)^{3/4}\left(\frac{W_0}{kT}\right)^{1/4}\right),$$

where r_{IC} is the length of the tunnel 'jump' of the electron equal to the distance between 'nanocarbon' clusters, σ_0 - normalization constant, which means the conductivity of monolithic dielectric medium.

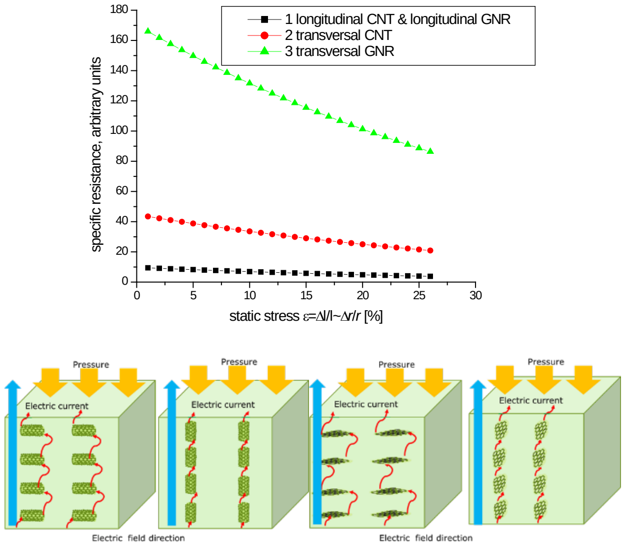

FIGURE 1 Specific resistance of CNTs and GNRs based nanocomposite (epoxy resin) via static stress. Below – variants of morphological orientations of nanocarbon inclusions.

The availability of temperature factor in the hopping conductivity formula allows to create a model of temperature nanosensors using similar electric responses.

3 Polymer nanoporous structures based bionanosensors

Since the sixties of the past century it is 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 (~ 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 them nanoscopic voids, the larger ones tend to aggregate towards carbonaceous clusters. Thus, emerging structural disorder along the tracks modifies their electronic behaviour (see Figure 2). In particular, a complicated biochemical kinetics of basic reaction of glucose detection depends on track qualities (e.g from track creation mechanism, foil material properties), enzyme (GOx) distribution on the track surface, geometry of etched track etc. All these factors are subjects of the nearest special research. Moreover, the detailed kinetics of reaction is the object of 3D-modelling for design of optimal geometry of nanosensor active space. This allows to create optimized 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 that the tracks penetrate through all the foil the conducting connections emerge between the foil front and back sides. The ion track technology is, in particular, directed towards biosensing applications. In this case the ion tracks are functionalized directly by attaching organic or bioactive compounds (such as enzymes) to their walls.

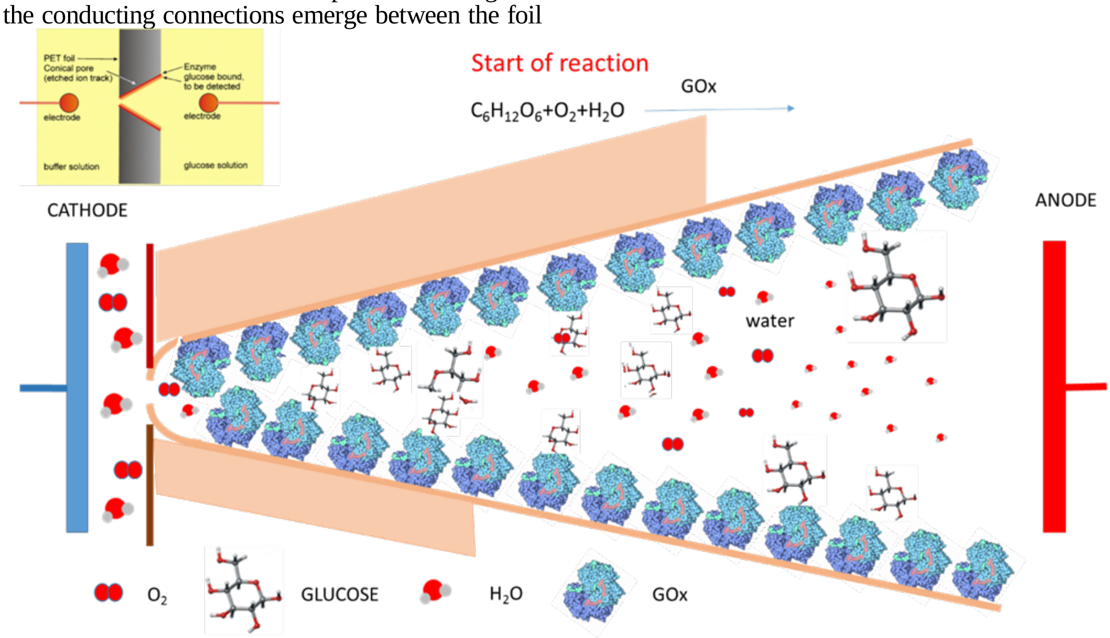

FIGURE 2 General scheme describing the detection scheme and modified polymer. Principle arrangement of experimental setup to study voltage-current dependences in ion track-containing foils embedded in electrolytes. The typical reaction for glucose indication:

$$\mathbf{C_6H_{12}O_6 + O_2 \xrightarrow{GOx} C_6H_{12}O_7 + H_2O_2}$$

$$\mathbf{H_2O_2 \xrightarrow{catalaza} \frac{1}{2}O_2 + H_2O}$$

$$\textbf{Anode: } \mathbf{H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-}$$

$$\textbf{Cathode: } \mathbf{2H^+ + 2e^- \rightarrow H_2}$$

$$\textbf{Ultimate reaction: } \mathbf{C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + H_2}$$

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

a) the overall net reaction is:

Glucose ($C_6H_{12}O_6$) + O_2 (due to enzyme-induced oxidation) $\rightarrow$ gluconic acid ($C_6H_{12}O_7$) + O;

b) This remaining O attaches to some H_2O to form peroxide H_2O_2;

c) the product: gluconic acid dissociates around pH=7: $C_6H_{12}O_7 \rightarrow C_6H_{12}O_7^- + H^+$; thus the liquid's conductivity changes (essentially if the product is enriched in the track's confinement); this is what is measured by the sensor.

The recent advances in this field allow monitoring and tracking biomolecules in areas such as environment, food quality and health. The presently developed ion track-based nanosensors provide high sensitivity, reliable calibration (Figure 3), low power and low cost [4, 5].

The creation of new biosensors and their further improvement requires a careful study of the mechanisms of electrolytes passage through the tracks.

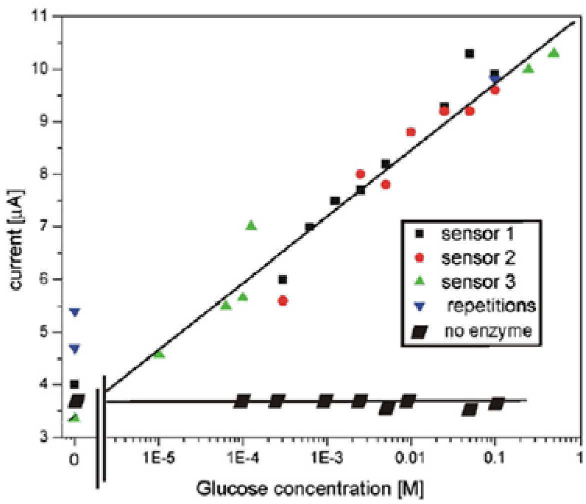

FIGURE 3 Performance comparison of three identically produced track-based glucose detectors against a calibration curve *I* (+5 V) vs. glucose concentration Current response to a pure buffer solution (i.e., glucose concentration = 0) is added on the left side. The standing triangles show for sensor the accuracy within which a measuring cycle can be repeated

4 Conclusions

- A nanocomposite pressure and temperature nanosensor prototypes has been simulated. The hopping conductivity mechanism gives the adequate description of possible nanosensor qualities. An important problem of manufacturing sensors based on CNTs and GRNs is nanocarbon inclusions orientation, which determines the electrical properties of the future sensor.
- Our work showed that iontrack-based glucose sensors can be easily created. Furthermore, they show good sensitivity, they cover the range of medical applications, and they can be reused at least 10 times. This study also shows that track-based biosensors with other enzymes can be similarly developed.
- Both nanosensoring schemes use the simple electrical responces outputs for device calibrations of parameters to be measured.

Acknowledgments

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