Self-presentation

1. First name and surname:

Paweł Szreoder

2. Diplomas obtained, academic degrees – including the titles, place and year of issue, and the title of doctoral thesis:

2004	Doctor of Physics (Ph.D.), Institute of Physics, Nicolaus Copernicus University in Toruń, the title of thesis: *Electron properties of carbon nanotubes*;
1999	Master of Philosophy (M.A.), Faculty of Humanities, Nicolaus Copernicus University in Toruń;
1992	Master of Physics (M.Sc.), Faculty of Mathematics, Physics and Chemistry, Nicolaus Copernicus University in Toruń.

3. Information concerning employment in scientific institutions;

2005 – 2014	Assistant Professor (in Polish nomenclature: adiunkt) in Institute of Physics, Nicolaus Copernicus University in Toruń;
04.2012 – 06.2012	postdoc position in Faculty of Mathematics and Natural Science, Ilmenau University of Technology, Germany;
08.2009 – 12.2009	postdoc position in Faculty of Mathematics and Natural Science, Ilmenau University of Technology, Germany;
2003 – 2005	Lecturer (in Polish nomenclature: wykładowca) in Institute of Physics, Nicolaus Copernicus University in Toruń;
12.1995	academic placement in Faculty of Natural Science, Chemnitz University of Technology, Germany;
1995 – 2003	Assistant (in Polish nomenclature: asystent) in Institute of Physics, Nicolaus Copernicus University in Toruń.

4. Indicating of the achievement pursuant to article 16 item 2 of the act of law dated 14 March 2003, concerning scientific degrees and scientific titles, and degrees and titles in the domain of arts (Official Journal No. 65, item 95 with later amendments):

(a) Title: **Physics of the interface of low dimensional carbons and ionic solutions**

(b) author: Paweł Szroeder, title of the monograph: *Physics of the interface of low dimensional carbons and ionic solutions*, Toruń 2013, Wydawnictwo Naukowe Uniwersytetu Mikołaja Kopernika w Toruniu, ISBN 978-83-231-3094-9

(c) Description of scientific objective of the above work and accomplished results, including description of their possible use.

4.1. Introduction

The monograph "Physics of the interface of low dimensional carbons and ionic solutions", which I have indicated as the main scientific achievement for habilitation proceedings, is a review of my research activity in the field of phenomena occurring in the interface connecting carbon nanotubes and graphene with ionic solutions. My contribution to deeper understanding of these phenomena relies on linking the kinetics of the electron transfer reaction occurring in the interface to the electron structure of low dimensional carbons and the interface structure of the ionic solution.

Electron band structure of nanotubes and graphene is comparatively well known. As a result of quantum confinement, van Hove singularities are present in the function of density of states of carbon nanotubes. An important characteristic of nanotubes and graphene is low density of electronic states near the Fermi level. The present state of scientific research with regard to the influence of disorder on the band structure of low dimensional carbons is advanced as well. Structural disorder induces localised electronic states in the vicinity of Fermi level.

The frontiers in research concerning the structure of electrolyte interface layer become more advanced, too. Results show that hydrophobicity of graphene plays the key role in the formation of the interface layer. Defects and support can change hydrophobic properties to more hydrophilic.

Despite of all this extensive literature concerning the electron band structure of carbon nanotubes and graphene, and interface structure of electrolyte adsorbed on carbon honeycomb lattice, there are still lacking reports, in which the task of determining the influence of both the factors on kinetics of heterogeneous electron transfer reaction is taken on. This was the main motivation for me to undertake these studies, which culmination is the presented mongraph.

Good surface conductivity, chemical stability, large active surface and biocompatibility of carbon nanotubes and graphene have key importance to use these materials in the construction of the next-generation efficient electrochemical devices. These devices can contribute to the development of cost-effective and precise medical and environmental diagnostics and small scale production of power.

4.2. Scientific objective

The aim of the monograph was systematic and, as far as possible, comprehensive presentation of the issues concerning the structure and processes, which occur in the interface of low dimensional carbons and ionic solutions.

My study is limited to carbon nanotubes and graphene. The common features of these materials are:

(i) hybridisation of electron orbitals, which enable the formation of flat honeycomb crystalline lattice;

(ii) quantum confinement being a consequence of the reduced dimensionality of crystals.

My objective was to investigate, how the density of states of low dimensional carbons can interfere with kinetics of heterogeneous reaction charge transfer. This applies particularly to:

- perfect graphene electrode and graphene with defects;
- perfect metallic and semicondacting carbon nanotube electrodes of different chirality;
- donor and acceptor doped carbon nanotube electrodes.

The consequence of the lack of dangling bonds in carbon honeycomb lattice and hydrogen bonding between molecules of water is hydrophobicity of perfect graphene. Therefore, a questions arise on:

- the influence of the structure of interface water on the kinetics of electrode reaction;
- the influence of substrate of graphene and nanoparticles of the transition metals, which are encapsulated in the central channels of carbon nanotubes, on the formation of interface structure connecting the electrode and ionic solution.

4.3. Achieved results

In my opinion, the most important point of my dissertation is **the linking the kinetics of the electron transfer reaction occurring in the interface to the electron structure of low dimensional carbons and the interface structure of the ionic solution**. My different contribution to the progress in the investigation of phenomena which occur at the electrode-electrolyte interface consists in:

(i) examination of the influence of **defect and and doping induced electron states** on the heterogeneous electron transfer reaction through the interface between electrolyte and low dimensional carbons. As a consequence, the enhanced electrocatalytical activity of graphene and nitrogen doped carbon nanotubes has been explained. Some results presented in the monograph has been published in [1, 2];

(ii) examination of the influence of **chirality of carbon nanotubes** on the kinetics of the electron transfer reaction. Some results has been published in [3];

(iii) demonstrating that graphene **substrate** and **iron nanoparticles** encapsulated in the central channels of multi-walled nanotubes enhances the kinetics of the electrode reaction;

(iv) determining the mechanism and range of **blocking of the electrode reaction** at epitaxial graphene using analyses of electrochemical impedance spectra. Results are published in [4];

(v) demonstrating that nitrogen doped nanotubes **catalyse the oxygen reduction reaction** in both the alkaline and acidic medium. I addition, I have shown that this material can be used for the construction of non-enzymatic **biosensors**. Results are published in [1, 5]. Till now, low dimensional carbons were considered as catalysts for oxygen reduction reaction only in alkaline media;

(vi) demonstrating the correlations between **the intensity of the defect induced Raman D band and the kinetics of the heterogeneous reaction of electron transfer**. Results have been published in [2].

The specified elements of my contribution have been described in details in parts 4.3.1 – 4.3.6 of the self-presentation.

The investigated low dimensional carbons were:

- single-walled carbon nanotube mats (BP from *buckypaper*), which were fabricated by me from single-walled carbon nanotubes delivered by Nanocyl®. The method of vacuum filtration of nanotube suspension in aqueous solution of SDS was used;
- carpets of non-doped multi-walled carbon nanotubes (MCNTs), which were grown in the Institute of Physics of the Ilmenau University of Techonlogy on Si/SiO_2 substrate by spray pyrolysis of benzene;
- carpets of nitrogen doped multi-walled carbon nanotubes (MN-CNTs). Here, acetonitrile, instead of benzene, was used as a precursor. Results of SEM-EDS investigations published by me in Ref. [1] show, that the concentration of the N atoms in MN-CNTs was of 7 at. % ;
- epitaxial graphene (EG), which was synthesised in the Institute of Electronic Materials Techonlogy (ITME), Warsaw, by thermal decomposition of SiC. Using this method, single- and few layer graphene was grown directly on the SiC substrate. Unique technology of the graphene growth invented in ITME is described in details by Strupiński et al. in [6];
- highly oriented pyrolytic graphite (HOPG). This bulk crystal was used as a reference material.

4.3.1. Influence of doping- and defect-induced electron states on the kinetics of electron transfer reaction

Electron structure of graphene and carbon nanotubes is presented in chapter 2.1 of the monograph. Classification of defects considering its impact on the density of electron states was described in chapter 2.2. The most important theoretical part of my work, in which the discussion of the simulations results concerning the kinetics of electrode reactions is reported, is given in chapter 3.3 of the monograph.

Simulations of the kinetics of electrode reactions have been carried out using the Gerischer model, which is described in chapter 1.3.2 of the monograph. Calculations have been performed for anodic reaction, where electron transfer between reduced form of electroactive species, $\mathrm{Fe(CN)}_6^{4-}$, and graphene/nanotube occurs.

In Fig. 1 the calculated dependence of the anodic reaction rate on the potential of perfect graphene is shown. Results presented in Chapter 2.2 of the monograph as well as the calculations carried out by Jaskólski et al. [7] show that zigzac edges and point defects induce additional states, which energy is close to the energy of the charge neutrality point ($\epsilon = 0$).

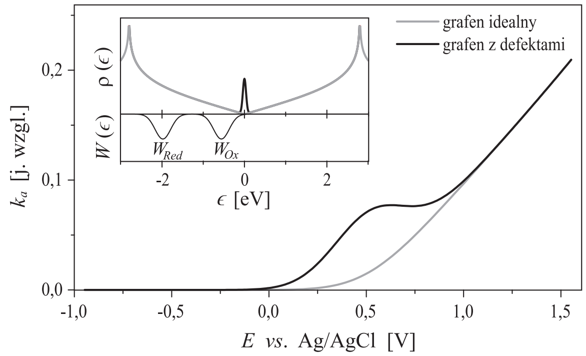

Fig. 1: Dependence of the anodic reaction rate between the electroactive species and graphene as a function of potential of graphene electrode. In the inset, the densities of states of the perfect graphene and graphene with defects are presented.

Assuming a Gaussian distribution of defect states of the half width of 0.1 eV, I have investigated the influence of disorder induced states on the electron transfer kinetics. After introduction of defect states, standard electron transfer rate constant[1] increases fifteen times.

To determine the influence of doping of carbon nanotubes on the kinetics of anodic reaction, donor and acceptor bands of width of 0.5 eV were introduced to the perfect metallic $(10, 10)$ and semiconducting $(17, 0)$ carbon nanotubes (see Inset to the Fig. 2a and b). The bands of the comparable width have been observed by Czerw et al. [8, 9] for nitrogen and boron-doped carbon nanotubes in the electron tunnelling spectroscopy experiments. Results of my simulations of the anodic reaction rate as a function of electrode potential are presented in Fig. 2.

Results of calculations performed by me show that:

- acceptor states stimulate the kinetics of electrode reaction more strongly than donor states;

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[1] Electron transfer rate constant is the reaction rate at formal potential, at which the cathodic and anodic reaction rates are equal. In case of reversible reaction, we can assume that formal potential is equal to the half-wave potential. I have determined the half-wave using the CV data for the reaction $\mathrm{Fe(CN)}_6^{3-} + \mathrm{e}^- \rightleftharpoons \mathrm{Fe(CN)}_6^{4-}$ to the value of $E_{1/2} = 0{,}2$ V vs Ag/AgCl

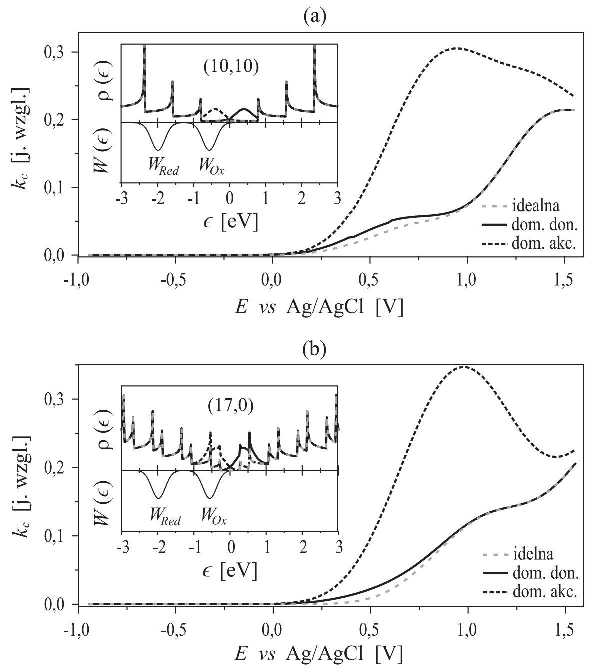

Fig. 2: Dependence of the anodic reaction rate as a function of the electrode potential for perfect carbon nanotubes as well as for donor and acceptor doped carbon nanotubes: (a) metallic nanotube, (b) semiconducting nanotube. In the insets, densities of electron states, for which the calculations were carried out, are presented.

- in metallic nanotubes, the standard electron transfer rate constant is almost doubled after introduction of donor states. Acceptor doping causes more than threefold increase of the standard rate constant;
- much stronger influence of doping on kinetics of electrode reaction is observed in semiconducting nanotubes. After introduction of donor states, the standard rate constant increases eighteen times. In the presence of acceptor states, more then forty-fold increase of the standard rate constant is observed.

I have confirmed experimentally the enhanced kinetics at donor doped nanotubes (chapter 3.1.2 of the monograph). Experimental value of standard rate constant at MN-CNTs is four times higher than standard rate constant at undoped MCNTs (see Table 1 in section 4.3.6 of the self-presentation).

Up to date, there are no experimental data allowing the statement if the acceptor doping enhances the electrocatalytic properties of low dimensional carbons. Results published by Salazar et al. [10] show rather blocking influence of acceptor doping on electron transfer kinetics. Salazar's findings contradicts the results presented by me. Further investigations are required for resolving the matter of the acceptor doping of low dimensional carbons and its connections with its electrochemical efficiency.

4.3.2. Chirality of nanotubes and electron transfer kinetics

The next question which I have considered using the Gerischer model was the influence of geometrical parameters of perfect carbon nanotubes defined by chiral vector (M, N) on the kinetics of electron transfer between the $\mathrm{Fe(CN)}_6^{4-}$ redox couple and the nanotube. Preliminary studies were presented in [3]. More detailed results of simulations of the dependence of anodic reaction on electrode potential are shown in chapter 3.3 of the monograph.

From results presented in Fig. 3 I have concluded that:

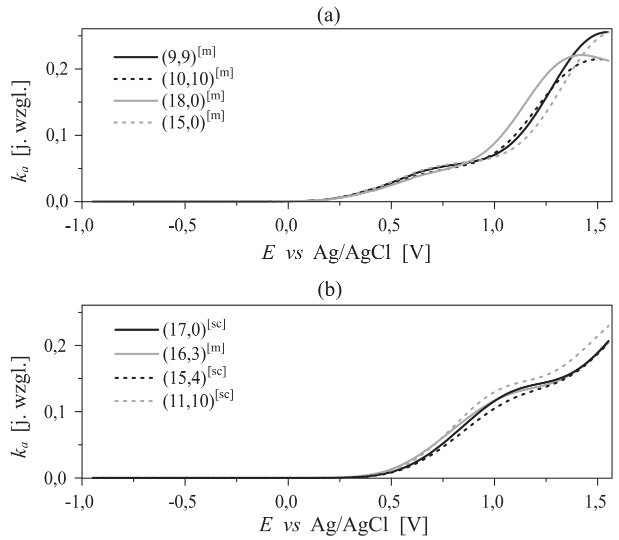

Fig. 3: Dependence of rate constant for the electron transfer from $\mathrm{Fe(CN)}_6^{4-}$ to carbon nanotube calculated using Gerischer model: (a) non-chiral metallic nanotubes. (b) chiral semiconducting and metallic nanotubes.

- all non-chiral metallic carbon nanotubes, i. e. armchair nanotubes with chiral vectors (M, M) and zigzac nanotubes with vectors $(3M, 0)$ show one type of dependence (Fig. 3a);
- another type of dependence is observed in chiral nanotubes, including both the semiconducting and metallic, with coordinates of chiral vectors of (M, N), where $M \neq N$, and in non-chiral semiconducting nanotubes (Fig. 3b);
- the standard electron transfer rate constant of nanotubes representing the second type of dependence is by one order of magnitude lower than the standard rate constant of nanotubes representing the first type of the dependence.

As it is very difficult to isolate individual nanotubes from ropes in which they are bonded by van der Waals forces, direct verification of the simulation is not possible. Analyses of Raman scattering spectra (chapter 2.4.5 of the presentation) show that BP is mainly composed of semiconducting nanotubes. Thus, experimental CV curves obtained for macroscopic BP result from averaging of the dependences of the rate constant, which are shown in Fig. 3b.

4.3.3. Influence of substrate and metal nanoparticles on the kinetics of electrode reaction

Experimental values of the standard electron transfer rate constant in the materials investigated varied by four orders of magnitude. Thus, the dispersion of experimental values is much larger than results of simulations which I have presented in section 4.3.1 of the self-presentation. Results presented in part 4.3.1 of the self-presentation show, that differences of the experimental values of standard rate constant are by two orders of magnitude higher than differences obtained from simulations. This is due to the hydrophobic nature of carbons bonded in honeycomb lattice. Interface water is an additional barrier for ions of electroactive species (chapter 2.3 of the monograph).

To support the claim, it is worth recalling results obtained by other authors. Theoretical value of standard electron transfer rate constant calculated by Royea et al. [11] for

$Fe(CN)_6^{3-/4-}$ redox couple and perfect semimetal was $2.8 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$. On the other hand, experimental value determined by Cline et al. [12] at pristine HOPG was lower by two orders of magnitude ($k_s = 1 \times 10^{-6}\,\mathrm{cm \cdot s^{-1}}$). But at anodized HOPG, where the structure of interface water is disturbed, I have obtained the standard rate constant, $k_s = 6.7 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$, which is comparable to the theoretical value calculated for perfect semimetal.

In my opinion, the change of the nature of HOPG from hydrophobic to more hydrophilic is the main factor, which contributes to the unblocking of electrode reaction. The changes are seen with the naked eye. I have observed that HOPG and EG after anodization became able to be wetted. Changes of the electron structure caused by functional groups attached to the electrode surface and defects induced during anodization plays rather minor role in the electron transfer kinetics.

The results presented show that the substrate can play the same role as the anodization. As it has been shown by Rafiee et al. [13], hydrophobic properties of graphene change to more hydrophilic under influence of substrate.

In systems investigated by me, electrode reaction efficiency is supported by:

- SiC substrate, which changes the properties of the anodized EG to more hydrophilic. Therefore the standard electron rate constant at the EG electrode ($27 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$) is four times higher than standard rate constant at anodized HOPG ($6{,}7 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$). Results obtained by other authors also show stimulating influence of substrate on kinetics of the electrode reaction. Valota et al. [14] have investigated graphene on the SiO_2 substrate. Results show higher value of the standard rate constant ($12 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$) compared to HOPG;

- nanoparticles of Fe in central channels of multi-walled nanotubes (see Fig. 2.16d in the monograph). Standard electron transfer rate constant was found to be $110 \times 10^{-4}\,\mathrm{cm \cdot s^{-}1}$ and $440 \times 10^{-4}\,\mathrm{cm \cdot s^{-}1}$, respectively, for MCNTs and MN-CNTs. Thus, the obtained values are higher by fairly two orders of magnitude than those found for HOPG.

Kinetics of the electrode reaction is also supported by nanoparticles of gold immobilized in the outer walls of MCNTs and MN-CNTs. Results of experimental studies, in which I have participated, are not included in the presented monograph. They are published in [15, 16].

4.3.4. EG as a partially blocked electrode

Results published by Biedermann [17] and Ohta [18] show non-homogeneous morphology of EG, where areas covered with buffer layer, G_0, are found together with the areas covered with G_0 and subsequent layers of intrinsic graphene, G_n. I have also observed non-homogeneous step-like topography of EG in AFM images.

I have shown that EIS spectra obtained for EG are characteric of the array of active microelectrodes, which are surrounded by inactive area (chapter 3.2.3 of the monograph).

Model curves obtained by me approximate experimental dependence of impedance on frequency of elecotrde potential with good accordance. On the base of fitting parameters, I have estimated the value of standard electron transfer rate constant for active surface of EG to $27 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$.

4.3.5. Nitrogen doped nanotubes as catalysts of oxygen reduction reaction and biosensor

Capability for catalysing the oxygen reduction reaction (ORR) is essential for using low dimensional carbons as an electrode material in fuel cells. I have performed tests of the catalytic activity of MCNTs and MN-CNTs towards ORR in aqueous solutions of KOH and H_2SO_4. Results are presented in chapter 3.1.2 of the monograph and have been published in [5].

They can be summarized in following sections:

- nitrogen doping leads to the reduction of overpotential, at which the ORR occurs;
- doping causes more than threefold increase of the reduction peak current. Its value is comparable with values obtained at noble metal electrodes;
- the electron transfer resistance, R_{et}, estimated from the EIS spectra obtained in the presence of oxygen is lower at MN-CNTs electode than at MCNTs. This indicates that nitrogen doping enhances the electrocatalytic activity of carbon nanotubes;
- high efficiency of nitrogen doped nanotubes in catalysis of ORR results from high electron affinity of nitrogen atoms in crystalline lattice of nanotubes.

I have also tested ORR activity of carbon nanotubes in aqueous solution of H_2SO_4. Results can be summarized as follows:

- in the presence of inert gas shield, considerable background currents at increasing and decreasing potential of the electrode are observed indicating high surface capacity of the electrodes;
- apparent ORR peak is observed only at MN-CNTs. Corresponding density of the peak current is three times lower than the one observed in alkaline medium;
- resistance R_{et} estimated from EIS data in acidic medium is higher than $1\,\mathrm{M\Omega}$. This gives an indication of low efficiency of MCNTs and MN-CNTs for ORR catalysis.

Analyses of EIS data show that accumulation of OH^- and H^+ occurs in, respectively, alkaline and acidic medium. This process is responsible for appearing of adsorption capacitance C_{ad} and resistance R_{sf}. They are additional factors blocking ORR. This particularly concerns the acidic medium, in which C_{ad} is by two orders of magnitude higher than in alkaline medium.

I have also studied electrochemical response to glucose and uric acid in aqueous solution of KCl at unmodified MCNTs and MN-CNTs. No response to glucose has been observed at both kinds of electrodes. In the presence of the uric acid, apparent oxidation peak appeared. Intensity of the oxidation peak was about twice higher at MN-CNTs electrode. Results of experiments shown in chapter 3.1.2 of the monograph were also published in [1].

4.3.6. Raman scattering spectra and electron transfer kinetics

I have recorded Raman scattering spectra of BP, MCNTs, MN-CNTs, EG and HOPG using excitation light of the energy of 2.54 eV (488 nm) and 1.17 eV (1064 nm). Results are presented in chapter 2.4.5 of the monograph and have been also published in [3].

To determine structural disorder in the materials investigated, I have used the intesity ratio of the D and G band. Part of results are published in Ref. [2]. All results are presented in chapter 2.4.7 of the monograph.

Using the Lucchese model [19] discussed in chapter 2.4.7 of the monograph, I have estimated the mean distance between defects, L_D. Reciprocal of the square of L_D is proportional to the surface density of defects, $\sigma_D \sim L_D^{-2}$. I have used this dependence for estimation of a number of defects per graphene unit cell, N_D, which area is of $5.24 \times 10^{-2}\,\mathrm{nm}^2$. The values of N_D are compared in the second column of Table 1.

$\mathrm{Fe(CN)}_6^{3-/4-}$ redox couple in aqueous solution and $\mathrm{FeCp}_2^{+/0}$ in organic solution have been used as electrochemical probes were used for estiamtion of standard rate constants. Such experimental techniques, as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) have been used. I have determined the standard rate constant using Nicholson procedure (chapter 1.4 of the monograph) or from the value of electron transfer resistance estimated from the EIS spectra (chapter 3.2 of the monograph). Details concerning the measurements and the results obtained are described in chapters 3.1 and 3.2 of the monograph. Part of results is published in [1, 3], where I am the first author, and in [20, 21]. Results are shown in column three of the Table 1.

Results obtained by me are compared to theoretical value of the standard rate constant calculated by Royea [11], experimental value obtained by Cline [12] for pristine HOPG, and experimental value obtained by Valota [14] for exfoliated graphene.

Table 1: Comparison of number of defects per graphene unit cell, N_D, and standard electron transfer rate constant, k_s. All the presented data have been obtained by me, except for: semimetallic electrode, unmodified HOPG and graphene deposited on SiO_2. Electron transfer rate constants were estimated for $\mathrm{Fe(CN)}_6^{3-/4-}$ redox couple. For MCNTs and MN-CNTs, $\mathrm{FeCp}_2^{+/0}$ has been used as an electrochemical probe.

	$N_D\,[\times 10^{-2}]$	$k_s\,[\times 10^{-4}\,\mathrm{cm}\cdot\mathrm{s}^{-}1]$	Ref.
Semimetal (theory)	0	2,8	[11]
HOPG	~ 0	0,01	[12]
BP	1,6±0,3	0,03	
Anodized HOPG	~ 0	6,7	
Graphene on SiO_2	b.d.	12	[14]
Anodized EG	36,8±3,6	27	
MCNTs	10,3±0,4	110	
MN-CNTs	12,6±0,4	440	

Data presented in Table 1 show following correlations between the defect density, structure of the interface layer of ionic solution and the electrocatalytical activity of low dimensional carbons:

- theoretical value of the standard electron transfer rate constant estimated by Royea et al. [11] for perfect semimetal is by two orders of magnitude higher than experimental value obtained by Cline [12] for pristine HOPG. This means that hydrophobicity of graphene and graphite is an essential factor which blocks the electron transfer reaction through the interface;

- value of the standard rate constant at the BP electrode, which is characterized by low defect density, is comparable with the value obtained for HOPG;
- value of the standard rate constant, which I have estimated for anodized HOPG, is by two orders of magnitude higher than the value obtained by Cline for pristine HOPG. Structure of the interface water is disturbed at surface of anodized HOPG making it more hydrophilic. However, structural changes in the surface of HOPG are not reflected in Raman scattering spectra;
- EG is a partially blocked electrode. Thus, the disorder parameter N_D does not reflect the relationship between the density of states and electrocatalytical activity of the EG elecotrde;
- comparison of standard rate constants at anodized HOPG and anodized EG shows, that substrate is another factor facilitating the electron transfer kinetics (see part 4.3.3 of the self-presentation);
- the best kinetics is observed at MCNTs and MN-CNTs, featuring a relatively high density of defects. Standard electon transfer rate constants are by one order of magnitude higher than at the anodized EG, by almost two orders of magnitude higher than at HOPG, and by four orders of magnitude higher than at BP and pristine HOPG;
- despite the fact that the estimated densities of defects in MCNTs and MN-CNTs are comparable, the standard electron transfer rate constant at MN-CNTs is four times higher than that estimated at MCNTs. This result confirms the stimulating influence of donor doping on the kinetics of electrode reaction;
- the next factor facilitating the kinetics of electrode reactions at MCNTs and MN-CNTs is the presence of Fe nanoparticles encapsulated in central channels of nanotubes (Fig. 2.16d, chapters 3.1.2 and 3.2.2 of the monograph).

4.4. Conclusions

Presented results of calculations and experiments enable me to formulate the following conclusions:

- as the results of simulations in Gerischer model show, dopant and defect states facilitate the electron transfer kinetics;
- standard electron transfer rate constant determined for single-walled nanotube mats, epitaxial graphene, and carpets of multi-walled carbon nanotubes changes from the value of $3 \times 10^{-6}\,\mathrm{cm} \cdot \mathrm{s}^{-1}$ to $2{,}7 \times 10^{-2}\,\mathrm{cm} \cdot \mathrm{s}^{-1}$. Correlations between the density of defects and electrode reaction kinetics are seen;

- hydrophobicity of graphene is the major inhibit factor for the efficiency of electrode processes. Interface water is an additional barrier for charge transferring through the interface;
- the structure of interface water adsorbed at graphene and graphite is disrupted after anodization. As a result, these materials become more hydrophilic;
- substrate is another factor facilitating kinetics of electrode reactions. Standard rate constant at the anodized EG is four times higher than the standard rate constant at HOPG;
- kinetics of the electron transfer reaction at carpets of multi-walled carbon nanotubes is clearly better if compared with the EG and HOPG. In this case, the iron nanoparticles encapsulated in central channels of nanotubes are the essential factor in enhancing of the electrocatalytic activity of nanotubes;
- carbon nanotubes doped with nitrogen catalyse the oxygen reduction reaction. This particularly applies to the alkaline electrolytes. While the overpotential, at which the reaction occurs, is higher than at the Pt electrode, the peak current density is comparable to the nobel metal electrodes. For this reason, carbon nanotubes can be an alternative to nobel metals in the construction of alkaline fuel cells;
- in epitaxial graphene there are areas with blocked electrocataytical activity. Inactive domains are covered with graphene buffer layer containing sp^1 and sp^3 bonded carbon atoms;
- submicroscopic structure of the double layer is reflected in the macroscopic quantities determined using ac impedance technique. The most important among them are the resistance of the electron transfer through the interface and double layer capacitance.

The following results obtained by other researchers provided the backdrop for all my achievements presented here:

- the structure of interface water adsorbed on graphene is typical to hydrophobic surface (chapter 2.3.1 of the monograph). Hydrogen bonding between the molecules of water and lack of dangling bonds play the major role in the formation of interface water;
- results of contact angle measurements performed by Rafiee at al. [13] show, that substrate can change the hydrophobic properties of graphene to hydrophilic (chapter 2.3.1 of the monograph). Rafiee's studies allow better understanding of my results, which concern the electron transfer kinetics at graphene and nanotubes with the encapsulated Fe nanoparticles;
- buffer layer of epitaxial graphene containing a high number of sp and sp^3 carbon bonded inclusions chemically bonds the closest lying water molecules (chapter 2.3.1 of the monograph). This issue was studied by Zhou et al. [22];

- carbon nanotubes and graphene can be used for: the construction of non-enzymatic biosensors (chapter 3.4.2 of the monograph) and enzymatic biosensors (chapter 3.4.3 of the monograph), the investigation of the redox reactions in proteins (chapter 3.4.4 of the monograph), the detection of oligonucleotides DNA (section 3.4.5 of the monograph), construction of the electrodes in supercapacitors (section 3.5 of the monograph).

4.5. Summary and perspectives

The monograph which I have indicated as a major scientific achievement, was dedicated to the matters of phenomena occurring at the interface connecting the low dimensional carbons and ionic solutions. To study these phenomena, I have used such experimental techniques as cyclic voltammetry and ac electrochemical impedance spectroscopy. Using experimental data I have determined the kinetics of the electron transfer through the interface, the resistance of the electron transfer and capacity of the double layer. I have examined the experimental results against results of simulations of the electrode reaction kinetics in the Gerischer model.

Part of my original results presented in the monograph was published in [1–5,20,21]. The most important issues which are published only in the monograph are results concerning the simulations of electron transfer kinetics through the interface.

In my opinion, significant contribution of the presented dissertation into physics of the interface of low dimensional carbons and ionic solutions consists in **linking the kinetics of the electron transfer through the interface to the electron structure of low dimensional carbons and the structure of the ionic solution interface**. The most important parts of my contribution could be summarized as follows:

(i) I have examined the influence of the defect and dopant states on the kinetics of the heterogeneous electron transfer reaction at interface of ionic solution and low dimensional carbon (part 4.3.1 of the Self-presentation);

(ii) I have examined the influence of the carbon nanotube chirality on the kinetics of electron transfer (part 4.3.2 of the self-presentation);

(iii) I have shown that both the substrate as iron nanoparticles encapsulated in the central channels of nanotubes can significantly facilitate the kinetics of the elecotrde reaction (part 4.3.3 of the self-presentation);

(iv) I have determined both the mechanism and the range of the blocking of electrode reaction at epitaxial graphene (part 4.3.4 of the Self-presentation);

(v) I have shown that carbon nanotubes doped with nitrogen catalyse the oxygen reduction reaction both in alkaline and acidic medium. Till now, low dimensional carbons were only considered as possible material for the construction of alkaline fuel cells (part 4.3.5 of the self-presentation);

(vi) I have demonstrated the correlations between the intensity of the disorder-induced Raman scattering D band and the kinetics of the heterogeneous electron transfer reaction (part 4.3.6 of the self-presentation).

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Results presented in the monograph are the starting point for further research. I am planning to extend the scopes of research by following issues:

- electrical switching phenomena in the systems of low dimensional carbons and electrolytes. Switching was observed in thin layers of amorphous carbon by Prof. Antonowich [23] in the 1970's. I expect that disorder induced states near the Fermi level of graphene and nanotubes can play the crucial role in the modulation of electrical conductivity;
- electrochromism, which lies in the reversible changes of optical properties accompanying with the redox reactions. I am going to study electrochemical systems with such electrochromic materials as graphene oxide, Prussian blue, conducting polymers immobilized on graphene and carbon nanotubes;
- electrochemical properties of low dimensional carbons with immobilized metal nanoparticles, as well as hybrid systems consisting of low dimensional carbons and biomacromolecules;
- examination of the influence of the edge defects on the electrode reaction kinetics at EG. Step-like morphology of the EG suggest that edge defects probably facilitate the electron transfer kinetics at EG;
- examination of the influence of the point defects on the kinetics of electrode reaction at HOPG, graphene, and carbon nanotubes. Point defects will be introduced into the structure by bombardment with high-energetic ions (cooperation with the National Taras Shevchenko University of Kyiv).

The exploitation of full potential of low dimensional carbons requires to resolve several practical difficulties. One of these is the development of the technology of graphene and carbon nanotube growth directly on substrates. I am planning to continue my research in this field.

The topics planned by me will be realized on the basis of the international cooperation, which is described in the part 5.3 of the self-presentation.

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5. Description of the remaining achievements

5.1. Description of the research activities before Ph.D. degree

I started my research work as a fourth-year undergraduate student in Department of Radiospectroscopy and Physics of Carbon Institute of Physics, Nicolaus Copernicus University under supervision of Prof. Dr. hab. Franciszek Rozpłoch. The subject of my Master's thesis was synthesis of fullerenes by dc arc discharge evaporation of graphite and analyses of their IR spectra [A1]. I graduated from Faculty of Mathematics, Physics and Chemistry in 1992. At the same time I started studying philosophy. In 1999 I wrote and defended my Master's thesis concerning ontological implications of Bell's inequalities [A2].

In September 1995 I started doctoral studies in Institute of Physics, Nicoalus Copernicus University. Soon afterwards (December 1995), I was employed for the post of Assistant in the Department of Radiospectroscopy and Physics of Carbon, Institute of Physics, Nicolaus Copernicus University. In that time, my research topics covered: the synthesis of single- and multi-walled carbon nanotubes and investigation the electronic properties of these materials. For nanotubes synthesis, I used the same arc discharge technique as for fullerenes. I also performed successful experiments with growth of carbon nanotubes on kanthal substrate using the CVD technique.

I characterized the synthesized materials using scanning and transmission electron microscopy, Raman scatering spectroscopy, IR absorption spectroscopy and XRD. I also investigated the electron localisation phenomena using electron paramagnetic resonance technique. Results were published in the [A3–A8].

In the predoctoral period I realised four university research grants, two of them as a coordinator. At that time I completed a short research internship at Chemnitz University of Technology funded by DAAD.

In March 2004 I defended Ph.D. thesis entitled "Electron properties of carbon nanotubes", which was written under supervision of Prof. Dr. hab. Franciszek Rozpłoch I defended [A9].

Before finishing my Ph.D. thesis I established the scientific cooperation with researchers from Institute for the Study, Restoration and Conservation of Cultural Heritage, Nicolaus Copernicus University in Toruń. We received funding from Committee for Scientific Research for the realisation of the research project "Elaboration of the dating method for the selected historical materials of organic origin by electron paramagnetic resonance and Raman spectroscopy", which was coordinated by Prof. Józef Flik. The effect of the cooperation were four publications [A10–A13].

My scientific achievements before my Ph.D. degree consist of 9 articles in peer-reviewed journals (1 indexed by WoS) and 6 articles in conference proceedings. Publications are presented in *List of scientiffic publications*, Annex 9. In addition, the results of my research work were presented during 16 conferences. My research activity was awarded in 2004 by Rector of Nicolaus Copernicus University (individual prize).

5.2. Description of research activities after Ph.D. degree

Directly after my Ph.D I continued my work in the Institute of Physics, Nicolaus Copernicus University. In 2005 I was employed for the post of adiunkt (assistant professor) in Department of Semiconductors and Carbon Physics, which was headed (and still is headed) by Prof. Dr.

hab. Franciszek Firszt. My research activity was focused on the issue of electron transport in low dimensional carbons and properties of graphite surface. I used such experimental techniques as: electron paramagnetic resonance, Raman scattering spectroscopy and IR absorption spectroscopy. Results of my studies were published in [A14–A16]. In the cooperation with researchers from Luminescence Dating Group, Institute of Physics, Nicolaus Copernicus University, I undertook studies on influence of the β irradiation on surface properties of HOPG. The result of collaboration were publications [A17, A18]. Another research, conducted in the cooperation with the Institute of Molecular Physics, Polish Academy of Science, Poznań, addresed the influence of the graphite lattice compression on the spectroscopic g factor in HOPG. Results are published in [A19, A20].

In that time, I continued scientific cooperation with researchers from Institute for the Study, Restoration and Conservation of Cultural Heritage under the Special Research Programme "Art conservation by lasers – analysis of Middle Age wall painting using spectroscopic and chemical techniques for art conservation". Results of investigations performed within this programme were published in [A21–A23]. After the completion of the programme, another multidisciplinary works were realised. Results are published in [A24–A27]. Another results of cooperation are 22 conservatory documentations and 3 expertises. My contribution to these elaborations concerned the analyses of vibrational spectra of samples of historical materials, analyses of the GPR profiles, and analyses of images obtained using several bands of electromagnetic radiation.

In 2009 I worked as a postdoctoral fellow at Ilmmenau University of Technology. During my stay in Ilmenau I undertook studies on properties of solid (diamond layers, carbon nanotubes) and liquid (ionic solutions) interface. I used cyclic voltammetry and ac imepdance spectroscopy techniques. Results are published in [A28–A30]. After return to Poland I continued the studies and extended them by modelling of the interface phenomena [A31, A32]. In 2012 I completed another internship in Ilmenau. During my second stay, I extended the studies on kinetics of electron transfer through the interface by graphene [A33]. I performed the series of tests of catalytic activity of low dimensional carbons towards ORR. This reaction occurs in fuel cells. Results are published in [A34].

A review of my research activity in the last years is the monograph [A35], which I have indicated as the main scientific achievement for habilitation proceedings.

My academic achievements after obtaining my Ph.D consist of the monograph mentioned above, 23 peer-reviewed articles (15 indexed by WoS), 13 articles in conference proceedings, one peer-reviewed chapter in the book published in Polish and Russian, and one peer-reviewed chapter in the book, which does not concern physics (see *List of scientific publications*, Annex 9). In that period of time, I delivered 13 presentations during international conferences. Results of my studies were preseted during another 11 conferences. I participated in 4 university grants, three of them I coordinated.

5.3. International cooperation

The outcome of two postdoctoral fellowships at Ilmeanu University of Technology (TUI) is the scientific cooperation with researchers from that university. In July 2013 I hosted in Toruń Dr. Nikos Tsierkezos from TUI. The result of his visit are two papers concerning the influence of gold nanoparticles immobilized on low dimensional carbons on their electrocatalytical activity [A36, A37]. Another visit is planned for September this year.

I also established the cooperation with Chemnitz University of Technology. Prof. Arved Hübler and Dr. Nora Wetzold, who are developing technology of carbon nanotubes printing on polymer substrate, were coordinators of the proposal *Integrated mass printed carbon nanotube sensors for environmental monitoring* (FP7-NMP-2013-SMALL-7). Although the project was not recommended to funding, result of cooperation is the paper [A38].

I also started the cooperation with Prof. Yuriy Prylutskyy (National Taras Shevchenko University of Kyiv), who is an outstanding specialist in the field of nanophysics and nanobiotechnology. Together with Prof. Prylutskyy we are planning to model and test experimentally the electron transfer phenomena in hybrid systems of low dimensional carbons and bio-macromolecules.

In September 2014 will held the 9th Torunian Carbon Symposium `http://www.fizyka.umk.pl/~tcs/2014/` will be held. I am the head of Organising Committee of this conference. This event provide an opportunity to extend the international cooperation.

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5.4. Miscellaneous research activity

After Ph.D. degree I was a reviewer for 11 academic journals indexed by WoS:

- Acta Physica Polonica A,
- Analytical Letters,
- Analytical Methods,
- Ionics,
- The Journal of Chemical Thermodynamics,
- Journal of Experimental Nanoscience,
- Journal of Nuclear Materials,
- Journal of Solution Chemistry,
- Nano,
- Physics and Chemistry of Liquids,
- Thermochimica Acta.

I was honoured by the prestigious **U.S.–Israel Binational Science Foundation** (BSF) with request for review of one research project. Numerous scientists participating in BSF programs have won prestigious awards such as the Nobel, Lasker, and Wolf prizes (`www.bsf.org.il`).

5.5. Achievements in the field of teaching

I am an academic teacher since September 1995. Till now, I have conducted computing classes, laboratory classes, computer classes, conversational lessons and lectures. Delivered courses are listed below.

1. Computing classes:
    - *General physics (mechanics)* for students of physics, applied physics, and astronomy;
    - *Physics* for students of chemistry, students of inter-faculty studies in chemistry and biology;
    - *Elementary physics* for students of materials of modern technologies and students of technical physics;
    - *Introduction into processing of measurements data* for students of physics, applied physics and astronomy;
2. Laboratory classes:
    - *Physics laboratory 1* for students of physics, applied physics, astronomy, automatics and robotics;
    - *Physics laboratory 2* for students of physics;
    - *Physics laboratory* for students of chemistry, biology and environmental protection;
    - *Electronics laboratory 1 & 2* for students of physics and applied physics;
    - *Laboratory of resonances and selected measurement techniques of solid state physics* for students of applied physics.
3. Computer classes:
    - DOS for students of physics;
    - $\LaTeX$ for students of informatics;
4. Lectures:
    - *Magnetic Resonances and Selected Measurement Techniques of Solid State Physics* for students of applied physics. The part of lectures concerning magnetic resonances is addressed to students of experimental and medical physics;
    - *Methods of studies on painting materials* for students of art conservation.

5. Conversational lessons on *History of philosophy* for students of physics, applied physics and astronomy.

The greatest achievements in teaching include preparing and realisation of the course of *Magnetic Resonances and Selected Measurement Techniques of Solid State Physics* addressed to students of applied physics. The course includes 30 hours of lectures and 30 hours of laboratory classes. The course topics cover a wide range of issues concerning measurement techniques widely used in industry, as well as the less available techniques, such as functional NMRI.

The next achievement, realised together with Prof. Jarosław Rogóż (Institute for the Study, Restoration and Conservation of Cultural Heritage, Nicolaus Copernicus University), are the lectures on *Methods of studies on painting materials* for students of art conservation. Now, the lectures includes 15 hours. Due to great interest in the issues presented in this course, it is planned to extend it to 30 hours. Complementary materials for the lectures are available in `www.fizyka.umk.pl/~psz/teaching.html`

I am the author of the chapter of a handbook *Issues of conservation and studies on architectural monuments* addressed to the students of architecture. The book was published in Polish and Russian.

I was a supervisor of 14 diploma theses (including 3 Master's theses, 3 Engineer's theses and 8 Bachelor's theses). At the moment, I am supervising one Master's thesis and one Bachelor's thesis. I was a reviewer of 17 diploma theses (including 5 Master's theses, 2 Engineer's theses, and 10 Bachelor's theses).

5.6. Achievements in the popularisation of physics

In 2000 I participated in preparation and realisation of Physics demonstrations for secondary students. I was a co-author of the following lectures given during Torunian Festivals of Science and Art:

- *Physics in the historical monuments preservation* (E. Basiul, R. Rogal, J. Rogóż, P. Szroeder, 2006),
- *In the cabinet of carbon curiosities* (P. Szroeder, 2009).

This and last year festival I participated in preparation and realisation of festival workshop about colors for younger children.

In my opinion, the major achievement in the popularisation of physics is the presentation *Time, space and movement – theatrical essay on physics, physical essay on theatre* (M. Bylicki, M. Giedrojć, P. Szroeder), which was prepared for the Festival of Science and Art in 2007. During that festival, the essay attracted about 800 spectators. Since that time another 5 presentations took place in several cities of Poland, which attracted an audience of over 2000 spectators, mainly high school students. Presentation in White Synagogue in Sejny (May 2011) was held under the patronage of the Polish Radio Two.

I reviewed the tasks for 11th Province Competition in Physics for secondary school students of the Kuiavia-Pomerania Province in 2013/2014.

5.7. Organisational achievements

Till now I have carried out following organisational works:

- since 2010, I am a coordinator of the course in *Elementary physics*;
- since 2008, I am a coordinator of the course in *Methods of studies on painting materials*;
- since 2007, I am a coordinator of the course in *Magnetic Resonances and Selected Measurement Techniques of Solid State Physics*;
- in years 2002 — 2009 I was an editor of the chronicles of Institute of Physics, Nicolaus Copernicus University.

During the 8th edition of *The Annual World Conference on Carbon*, which was held in Kraków in 2012 (800 participants), I was a member of the Local Advisory Committee. During that conference I chaired one of the sessions.

Since 1995 I have participated in the work of Organizing Committee of the Torunian Carbon Symposium. Currently, I am a chairman of the Organizing Committee of the 9th Torunian Carbon Symposium.

I am a member of the Polish Physical Society (PTF) and Polish Carbon Society (PTW). Since 2009 I have been a member of the Polish Carbon Society Board, since 2013 I have been the Vice-President of that society.

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The listing of my published scientific papers and/or creative professional works with information concerning educational achievements, scientific cooperation and promotion of science is presented in Annex 7.

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