Abstract

The present work is devoted to the study of the effects of aqueous solutions of NaCl, HCl, NaOH, KCl and HNO_3 on the optical and electrical properties of graphene and the generation of an electrical signal in graphene under the influence of flowing solutions.

The first part of the work (Introduction) explains all the theoretical issues related to the subject under discussion. First, the general properties of graphene and methods of its production are described (Chapter 1.1). The next Chapter 1.2 is devoted to the measurement techniques for studying the properties of graphene used in this work. A description of the interpretation of Raman spectra allowing the determination of the concentration of free carriers, stresses or the defect state of graphene can be found in Chapter 1.2.1. In turn, how to determine the concentration of free carriers and their mobility from Hall effect measurements can be found in Chapter 1.2.2.

A detailed description of how the electric charge is distributed at the interface between a solution and a submerged object, that is, how the so-called double layer is formed, based on various theoretical models, is given in Chapter 1.3.

The next Chapter 1.4, is concerned with the description of possible processes causing the generation of an electrical signal in graphene and carbon nanotubes induced by the flow of solutions, based on the available scientific publications.

The experimental part of the dissertation begins with a description of the measurement systems used in the study. Chapter 2.1 includes a description of the commercial measurement apparatus used during the study of graphene properties, i.e. the system for measuring the Raman effect and Hall effect, and the system for flow studies that was espescially developed. The samples used along with their parameters and the method of preparation for the measurements are presented in Chapter 2.2.

The results concerning the effect of aqueous solutions on the optical and electrical properties of graphene are presented in Section 2.3. The first section describes the samples used in this part of the work and the route taken by each sample, including their initial preparation, the measurement techniques used and how their contact with the solutions was realized (Chapter 2.3.1). The following sections describe the results obtained for all the solutions used. The first to be described is the effect of bringing graphene in contact with NaCl aqueous solution,

additionally subdivided into samples prepared by CVD (Chapter 2.3.2.1) and by sublimation (Chapter 2.3.2.2). The observed changes in the properties of graphene, in the case of NaCl solution, were small, which is promising from the point of view of stable generation of electrical signals in graphene. Intersting is the enhancement of the Raman signal, which can be explained by a SERS-type effect, or by passivation of defects responsible for excitation transfer. The following sections are concerned with describing the effects of the following solutions on the properties of graphene: HCl (2.3.3.1), NaOH (2.3.3.2), HNO_3 (2.3.3.3) and KCl (2.3.3.4). In the case of aqueous HCl solution, the occurrence of an intercalation process of graphene buffer layers was observed, which is a very interesting and unexpected phenomenon. From the point of view of applications in flow measurements, this implies the need to prepare samples in advance so that they do not intercalate during measurements. However, the observed effect can be used for intentional intercalation and fabrication of graphene monolayers and bilayers on SiC substrates. Next is a summary of the results so far and their analysis in terms of flow studies (Chapter 2.3.4).

The last Chapter (2.4) is devoted to the issue of the generation of electrical signals caused by the flow of aqueous solutions near the graphene surface. A typical measurement cycle repeated in the following chapters of the work is described first, highlighting its most important elements (Chapter 2.4.1). Using the results obtained in a number of measurements, the best configuration of the measurement system and sample preconditioning process was chosen, along with an explanation of such a choice, and a cross-section of the tested parameters and settings during all the experiments carried out is shown (Section 2.4.2). Among the key elements of the system was the use of additional electrodes - a working electrode and a reference electrode. The use of additional electrodes allows control of the parameters of the double layer, and thus has a critical impact on whether electrical signals can be generated in a given sample under the influence of the flow of aqueous solutions, and explains many of the ambiguities and contradictions reported by various research groups. Sample preparation is also important, particularly the use of graphene leads in place of previously used metallizations to avoid electrochemical processes.

Chapter 2.4.3 proposes to divide the measured signal into three components: static, flow and directional. The next subsections deal with the description of each of these components, taking into account the possible cause of their origin. Subsection 2.4.4 attempts to explain the general behavior of the waveform of typical signals generated on the measured samples in relation to the electrical double layer and the use of additional external current sources that modify the

parameters of the double layer and the charge transfer processes between the solution and graphene, resulting, for example, from surface defects.

Subsection 2.4.4.1 analyzes the signals depending on the direction of solution flow and provides a description of the experiment to confirm the presence of the " drag effect" in the measured signals.

The next Chapter (2.4.5) presents a detailed analysis of the effect of additional electrodes on the charge distribution in the double layer. It is shown how fundamental it is to the generation of signals in graphene to obtain an appropriate charge distribution of the double layer. Thus, the ability to control it turns out to be crucial. The dependence of the results obtained on the double layer is best demonstrated by the proposed and described method of separating the flow direction-dependent signal from the total measured signal in Chapter 2.4.6. It exploits the observation that the flow direction-independent component of the generated signal is related to charge transfer to graphene from solution, and by measuring the current flowing through the working electrode it can be extracted from the total signal. This is the key element that is the problem of many works dealing with the subject of signal generation in graphene under the influence of flowing liquid.

The velocity dependence of both the whole signal and only its directional part is presented in the next Chapter (2.4.7.). An attempt has been made in this chapter to explain the occurring dependence of the magnitude of the generated signal on the velocity of the solution. The effect of the concentration of the aqueous solutions used is described in Chapter (2.4.8).

The results obtained provide information on the practical possibilities of using graphene sensors to measure the flow velocity of various solutions, which may be relevant both for specific technical applications and in microfluidics, important for medical and biological measurements. The last included chapter summarizes the entire work.