



PhD Proposal: Amphiphilic DNA molecules for dispersion of graphene for supercapacitor devices

1. Title of the Project

Amphiphilic DNA molecules for dispersion of graphene for supercapacitor devices

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4. Abstract

The decrease of fossil fuels generated an intensive search for alternative natural energy sources. The introduced Lithium-ion batteries, even with recent modifications, do not have the desired efficiency in applications; specifically the full charge/discharge time takes up to an hour, which is too long for electronic systems. This problem can be overcome by supercapacitors, based on graphite materials. These storage devices with big capacitance properties were proposed just recently and have attracted great attention from scientists as an alternative storage media [1-2]. Especially graphene, which has been the focus of many recent studies as well, is in particular suited for such devices due to its high surface-to-volume ratio. It was shown, that sandwich graphene structures as supercapacitor contacts helps to increase the capacitance value of devices, but the production of such well-defined sandwich structures is still a challenging goal. On this proposal we present a conceptual new approach for the fabrication of graphene sandwich structure that is based on a DNA amphiphile and the fabrication of graphene multilayers by hybridization. DNA modified with π -conjugated molecules allows for good graphene dispersion, selective self-assembling properties with a possibility to the control pore and gap sizes via the DNA chain length. The proposed method is less



expensive than Chemical Vapor Deposition (CVD) and gives new opportunities for innovative research in the field of supercapacitors in combination with nanobiotechnology.

5. Duration of the project

4 years, starting from September 2011

6. Personnel

The proposal is designed for one PhD student who will be supervised by Prof. A. Herrmann, the leader of the research group Polymer Chemistry and Bioengineering at the Zernike Institute for Advanced Materials.

7. Cost Estimates

		2011	2012	2013	2014	Total
Position	PhD student	1	1	1	1	
	Personnel	37	37	37	37	148
	Consumables*	10	10	10	10	40
	Equipment	0	0	0	0	0
	Total	47	47	47	47	188

*Consumables represent solvents, phosphoramidites, Si substrates, AFM cantilevers and AFM sample substrates.

8. Research Program

8.1. Introduction

Sustainable and renewable energy sources have attracted great interest nowadays due to the decrease of natural reserves. There fore, the possibility to collect energy from wind, sun, water etc. is a subject of extensive research. A big drawback of these sources is the time periodicity of energy generation, for example a change of sunlight from day to night and wind is not blowing continuously. Due to this fact energy storage plays an increasingly important role and the development of powerful energy storage devices is one of the most challenging goals for the scientists in the near future.

The main types of energy storage technologies are batteries and electrochemical capacitors (ECs). Despite a high price of Lithium-ion batteries, they are widely used and provide storage energy densities up to 180 Watt hours per kilogram. Nevertheless, the time of the charge/discharge process still takes up to an hour even for the most improved Lithium-ion batteries, which is a drawback for application as fast sources [3]. The desired high speed sources have been achieved with ECs devices, where the capacitors can be charged-discharged in a few seconds, i.e. such capacitors with storage possibility of 5 Watt hours per kilogram can produce an energy power of 10 kWatt hours per kilogram in a few seconds. This advantage of EC motivates their further



development for energy storage. The capacitance power of such ECs can be increased drastically via enhancement of the surface area of working contacts, where graphene is an excellent candidate. The preparation of such large surface carbon contacts for storage of more carriers and a study of their behavior inside the devices during the process of charge/discharge are important directions for the improvement of new capacitor storage possibilities. There are three groups of ECs devices: electrochemical double layer capacitors (EDLCs), pseudo-capacitors or redox supercapacitors and hybrid capacitors, which implement the two previously mentioned principles together. The EDLCs are especially appealing due to their natural high operation speed in comparison with other types of capacitor devices. The development of such devices is the subject of this proposal.

8.2. Goal of the proposal

We would like to propose an easy and low cost technique for well-ordered graphene sandwich structure formation with precise separation of the graphene sheets for EDLCs device contacts. Our approach has the following advantages in comparison with other established techniques.

1. We propose the use of a graphene dispersion technique in aqueous solution that circumvents the chemical modification of graphene and preserves the unique high transport properties of pristine graphene sheets.
2. Bis(pyrene)-DNA molecules used as dispersion agent make it possible to control the pore distance between graphene sheets and to avoid the problem of their restacking during charging/discharging cycles due to the presence of double stranded DNA spacer.
3. The tuning of the pore size between graphene sheets via DNA length control of bis(pyrene)-DNA molecules makes it possible to study the poorly understood dependence of ion mobility during charging/discharging cycles, for different ionic liquids.

Further studies regarding capacitance properties using the proposed technique will be carried out by involving redox active molecules in the graphene DNA dispersion to implement a pseudo-capacitance functionality between graphene sheets. This investigation of hybrid systems is promising as the next step of for increasing capacitance of supercapacitors preparation technique proposed here.

8.3. EDLCs supercapacitors

The first electrochemical capacitor based on carbon material with an understood working concept was patented in 1957 by Becker [4]. The high specific surface area (SSA) of the capacitor was prepared by deposition of carbon on a metallic current collector, where charge storage was measured in a sulphuric acid solution. The generation of an aqueous-electrolyte capacitor was developed first in Japan in 1971 by SOHIO Energy Company, which introduced the application of capacitors in commercial devices.



Let us consider the main principles of EDLC devices and methods of their development proposed here. The EDLC device is constructed as a battery with two electrode surfaces immersed in an electrolyte with a permeable ion separator between the two, Figure 1. The two sides of the cell capacitor can be interpreted as two separate capacitors with an electrode-electrolyte interface, where the full capacitance value of a device equals to their inverse sum.

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

where C_1 and C_2 are the capacitances of the first and the second electrode, respectively. The capacitance of such a double layer at each electrode is dependent on ϵ the dielectric constant of the electrical double-layer region, A the surface-area and t the thickness of the electrical double layer in the following way:

$$C_{double_layer} = \frac{\epsilon A}{4\pi t} \quad (2)$$

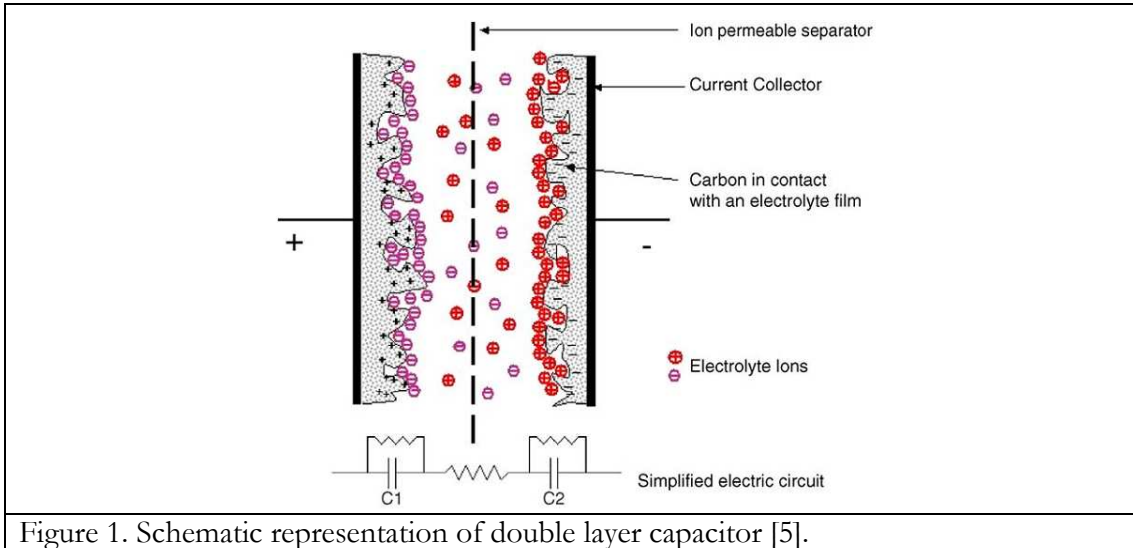


Figure 1. Schematic representation of double layer capacitor [5].

As it is shown in Eq. 2, the value of the double layer capacitance linearly increases with the surface area of the double charge density layer, which is one way for super high capacitance increase [6]. The energy E and power P_{max} of a capacitor can be calculated as:

$$E = \frac{1}{2} CV^2 \text{ and} \quad (3)$$

$$P_{max} = \frac{V^2}{4R} \quad (4)$$

where C is the dc capacitance in F , V is a voltage in Volts and R is an Equivalent Series Resistance (ERS) in Ohms. Pore size, surface contact area and properties of ionic liquids are the main factors for the determination of the device capacitance.

The type of working electrolyte plays an important role. For instance, the aqueous electrolytes such as acids (e.g., H_2SO_4) and alkalis (e.g., KOH) represent high ionic conductivity and relatively low decomposition voltage of ~ 1.23 V. The non-aqueous electrolytes such as propylene carbonate or acetonitrile have a higher decomposition voltage up to ~ 2.5 V. The inherent advantage of an aqueous electrolyte is a low dielectric constant in comparison with a non-water based solution, which essentially increases the



cell capacitance at the same structural conditions. The resistance of capacitances of non-aqueous electrolytes is one order higher a aqueous electrolytes in general, due to the corresponding high electrolyte resistance.

The way to increase capacitance energy (3) and power (4) of devices is to use electrolytes with high decomposition voltage, which enables drastic increase of the charge density at the double layer. Ionic liquids are good candidates for such replacement with electrochemical window up to ~ 7 V and with an excellent thermal stability in the range from -40 to $+200^\circ\text{C}$, which is proposed in this scientific research program.

Another combined strategy for capacitance increase is to increase surface contact with electrolyte at the capacitance contacts. An excellent candidate for this is graphene material with the highest surface area up to $2675\text{ m}^2 / \text{g}$. The application of a graphene surface in capacitors preparation has recently increased and is being widely studied. One of the main questions is: how to generate a homogeneous porosity for capacitor's contacts with full surface excess of electrolyte ions? The question of the optimization of pore sizes for maximum energy storage and fast ion mobility is a challenge as well. These problems will be solved in this proposal.

8.4. Porous graphene contact fabrication

Porosity of capacitance's contacts has a big influence on the capacitance value due the increase of the effective surface area for charges storage. Application of activated carbon (AC) materials with increased porosity or carbon nanotubes (CNTs) for contact formation showed good stability for EDLC devices but not a tremendous increase in the capacitance [7-8]. Random micropore formation with bad or completely closed excess to charge carriers is the main problem of low charge storage at the capacitor walls. Device capacitance can be increased by chemical modification of the wall contacts with charged polymers or redox active proteins.

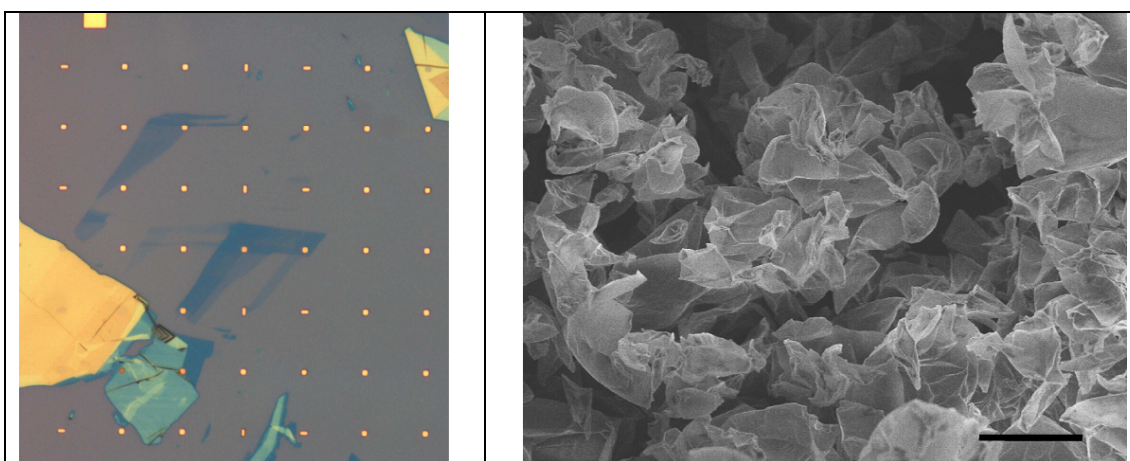


Figure 2. (left) Picture of different graphene flakes on Si substrate deposited by scotch tape technique. (right) Curved graphene flakes as pore material for supercapacitor devices (TEM image) [16].

However, this method helps to increase charge storage values with low charge/discharge time, which is not desirable for fast electronics [8]. This problem can be overcome via increasing contact surface and their geometry optimization. Large surface contact area with well ordered porous structures allows for an increase of a device charge storage and



mobility of carriers during charge/discharge cycles. Properly chosen materials and methods for capacitance contact formation is the main goal of our proposed research study.

As mentioned before, an ideal candidate for such contacts is a single layer graphene sheet. It is a 2D hexagonal lattice of sp^2 carbon atoms covalently bound in honey comb lattice, where a single layer graphene sheet can be distinguished from multilayer by an optical microscope which is convenient for device preparation, Figure 2 (left). The high surface to volume ratio, high strength, thermal and electrical conducting properties make graphene the best candidate for supercapacitor contact formation [10-13]. Currently the graphene based EDLC devices allow for reaching a maximum possible value of capacitance equaling $21 \mu F / cm^2$ [14]. The novel capacitance properties of graphene were first reported in 2006 by Dr. Jang's research group [1, 2] and became a starting point for graphene application in supercapacitor devices.

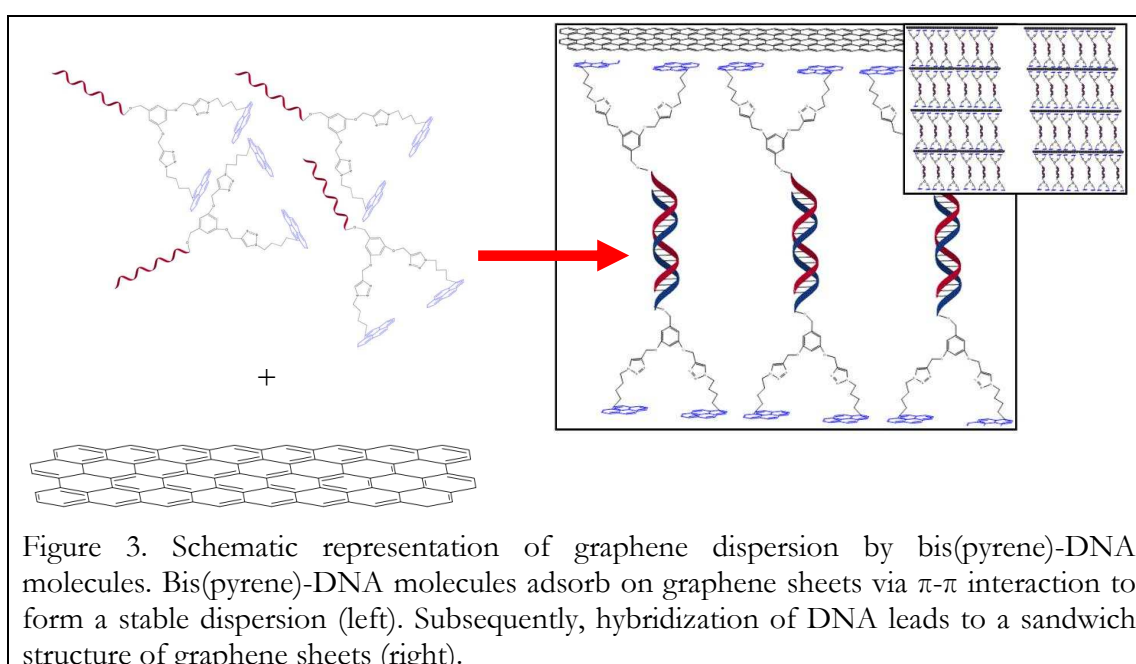
Another way of increasing the capacitance of a device is the proper choice of the electrolyte solution. The application of ionic liquids with wide voltage operating window allows increasing the mobility of charge carriers without solute dissociation, as it happens for aqueous electrolytes. The study of ionic liquid was initiated by Rao et al. They have shown a capacitance energy density increase up to 31.9 Wh/kg for $60 C^\circ$ [15]. Nevertheless, essential improvements were achieved again in Dr. Jang's group for curved pristine graphene sheets in EMIMBF₄ ionic liquid solution, which underlined the importance of proper combination of contact porosity and ionic liquids, Figure 2(right). An capacitance value of 85.6 Wh/kg at a current density of 1A/g at room temperature, was the highest EDLC value ever reported without pseudo-capacitance contributions (equivalent to that of Ni metal hydride battery and being completely recharging in less than 2 min). [16]. As was mentioned before, the expected high capacitance value was limited by ill-defined pores, which are not accessible was described for large ionic liquid molecules. Later the importance of graphene sheet spacing and orientation at the capacitor contacts for ion mobility during charge/discharge cycles [17, 18]. The idea proposed here allows optimization of these parameters to the possibility of plane orientation of graphene via the here proposed DNA-mediated self-assembly mechanism.

8.5. DNA graphene dispersion

In this proposal we introduce a new method of sandwich graphene formation with controlled separation distance for super capacitor device preparation. The well ordered graphene sheets construction can be prepared directly from high oriented graphite carbon (HOPC) or graphite powder via dispersion by 1-pyrenecarboxylic acid (PCA) and of bis(pyrene)-DNA molecules [19]. The noncovalent exfoliation proposed here can be done with a help of the 1-pyrenecarboxylic acid (PCA) molecules in a polarity-controlled solution [19]. The energetically favorable π - π interaction between graphene and pyrene in a polar environment and the hydrophilic -COOH group of PCA make an excellent stable aqueous dispersion of single graphene sheets. 3D structure formation of graphene flakes is carried out by hybridization of single stranded DNA of bis(pyrene)DNA molecules introduced during the dispersion process or after PCA dispersion. The separation between graphene sheets in sandwich structures can be easily adjusted by the length of the DNA. Our group has a long studying experience in the fabrication of carbonaceous material dispersion with the biomolecule DNA. In previous experiments single walled carbon nanotubes (SWNT) were dispersed with a conjugate



consisting of an oligonucleotide unit and a conjugated polymer segment and subsequently SWNT field effective transistor devices were fabricated in extraordinary high yield of 98% mediated by the DNA code [20]. The chemical synthesis of bis(pyrene)-DNA was previously carried out in our group, which is the first stage for supercapacitor device preparation. The bis(pyrene)-DNA conjugate consist of two pyrene units that are coupled via a linker moiety to a 22 mer oligonucleotide sequence. The schematic representation of pyrene dispersion with bis(pyrene)-DNA molecules is represented in Figure 3. The bis(pyrene)-DNA molecules attach to graphene sheets via π - π interaction, while the DNA sequence protrudes away from the sheet to introduce compatibility with the aqueous environment. On a subsequent step two graphene sheets dispersed with complementary sequences are assembled by hybridization to form a 3D-sandwich structure.



8.6. Graphene supercapacitor device fabrication

Fabrication and characterization of double-layer graphene sandwich structure. Graphene dispersion is directly fabricated from graphite powder by sonication in a solution of 1-pyrenecarboxylic acid (PCA), methanol and distilled water [19]. An excess of unbound PCA can be removed by centrifuging several times, and the concentration of PCA molecules is determined by UV absorbance measurements and Transmission Electron Microscopy (TEM) analysis. Atomic Force Microscopy (AFM) is applied for characterization of single-layer graphene dispersion by transferring dispersion solution on a mica surface. The double-layer graphene sandwich structure introduced by introduction of bis(pyrene)-DNA molecules. By Scanning Electron Microscopy (SEM), TEM and AFM the double-layer structure of the sandwich will be detected.

Fabrication of sandwich structure in graphene devices. The sandwich graphene film can be reduced in width and removed from the prefabrication zone by using a sharp razor blade. Sputtering equipment is used for gold contact deposition via a



home made mask where the working area is prevented from deposition. The scratch between two contacts can be made by a sharp razor blade as well to create a gap of a few tenths of micrometers for electrolyte excess and proper insulating between two electrodes.

Electrochemical Characterization. The galvanostatic charge/discharge time and cyclic voltammetry measurements can be done by using both AUTOLAB PGSTAT 302N and Princeton Applied Research Bistat of two probe systems. The schematic structure of graphene-DNA supercapacitor sandwich structure device is shown in Figure 4.

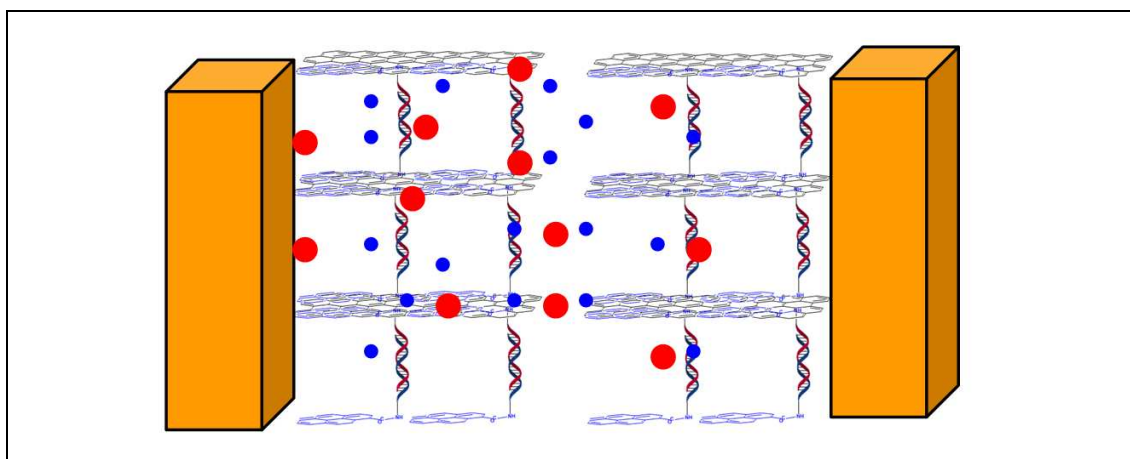


Figure 4. Schematic representation of graphene sandwich structure device. The graphene sheets are organized in sandwich structure with help of bis(pyrene)-DNA molecules. The ionic liquid ions and cations are represented as red and blue spheres, respectively.

9. Project Timeline

First year: Resynthesis of bis(pyrene)-DNA molecules for stable graphene dispersion in aqueous environment. Optimization of single graphene flakes dispersion by varying the bis(pyrene)-DNA molecules and PCA concentration as well as exploiting different dipole environment.

Second year: Optimization of the procedure of sandwich structure formation with a controllable number of graphene layers and pores. Sandwich structure preparation with different pore sizes via bis(pyrene)-DNA molecules. Investigation of the mechanical and time-dependet stability of sandwich structures.

Third year: Preparation of supercapacitor devices with well ordered graphene pore contacts and charge capacitance properties characterization. Study of the charge carriers mobility in devices as a function of layer spacing size and size of ionic liquids molecules. Determination of the stability properties of the supercapacitors under multiple charge/discharge cycles.

Fourth year: Preparation of hybrid graphene based devices with both a double layer capacitance and pseudo-capacitance via application of oxidation/reduction active molecules in a sandwich structure device. Determination of storage limitation,



charge/discharge time and stability properties under cycling of the hybrid supercapacitor devices.

10. Infrastructure

The Zernike Institute for Advanced materials provides a variety of processing and measuring facilities. For this project the most important facilities are:

- A DNA synthesizer for bis(pyrene)-DNA molecule preparation is available in the Herrmann group as well as other equipment for the preparation of graphene dispersions.
- An atomic Force Microscope (AFM) to study the quality of graphene dispersions from graphite powder is present in the Herrmann group.
- The porosity of graphene sandwich structures will be measured by Scanning Electron Microscopy (SEM) provided by NanoLab Groningen and Transmission Electron Microscopy (TEM) available with Material Science group (leader Prof. Dr. J.T.M. De Hosson).
- Sputtering equipment for contact preparation of supercapacitor devices is as well provided by NanoLab Groningen.
- Electrochemical measurement of the devices will be realized in group of Physics of NanoDevices, (leader Prof. Dr. Bart van Wees).

Standard laboratory equipment for chemical synthesis and glassware are readily available in the Polymer Chemistry and Bioengineering (PCBE) group.

11. Application Perspectives

The mechanism of sandwich structure formation for supercapacitor devices that we propose here is a novel and promising method for increasing device energy storage. It is possible to create a parallel graphene structure with excellent electrical properties without expensive and time consuming techniques, such as Chemical Vapor Deposition (CVD). The conducting properties of DNA chains between two neighboring graphene sheets can be used as an extra tool to induce homogeneous charge distribution along pore contacts of the supercapacitor. Undoubtedly, this method will allow for comprehensive studying of ionic liquids and graphene space orientation for supercapacitance devices. The convenient technique has high potential for industrial application for energy storage systems. Finally, this method will make it possible to conduct a comprehensive study of ionic liquids in graphene sandwich structures for the preparation of supercapacitance devices as a function of graphene space orientation.

12. References

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