



# TEKSTİL VE MÜHENDİS

## (Journal of Textiles and Engineer)



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### Projection of Sciences Onto Textile and Fashion: Nano-Technology and Chargeable Fabric Example

### Temel Bilimlerin Tekstil ve Moda Üzerine İzdüşümü: Nano-Teknoloji ve Şarj Edilebilir Kumaş Örneği

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Online Erişime Açıldığı Tarih (Available online): 30 Mart 2015 (30 March 2015)

#### Bu makaleye atıf yapmak için (To cite this article):

Özgür ÇOBANOĞLU, Jitka ERYILMAZ, Mehmet Fatih ATAŞALAN, Semih KAZANÇ (2015):  
Projection of Sciences Onto Textile and Fashion: Nano-Technology and Chargeable Fabric Example,  
Tekstil ve Mühendis, 22: 97, 21-30.

For online version of the article: <http://dx.doi.org/10.7216/130075992015229704>



***Research Article / Araştırma Makalesi***

# PROJECTION OF SCIENCES ONTO TEXTILE AND FASHION: NANO-TECHNOLOGY AND CHARGEABLE FABRIC EXAMPLE

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**ABSTRACT:** This proceeding provides readers with an overview of our multidisciplinary approach to technical textile research through reviewing recent preliminary results of an example project aiming at developing super-capacitor fabric structures. The fundamental idea of the project is based on, production of graphene nano-sheets and their application onto textile fabric, growing the oxides of manganese on graphene coating and utilization of the final fabric within a suitable electrolyte as electrode material. Graphene nano-sheet production and characterization methods, application to textile fabric and surface resistance measurements as well as construction of super-capacitor architecture and characterization of the final device capacitance via electro-chemistry are presented.

**Keywords:** Nano-technology, graphene, super-capacitor, wearable technology, storage, battery

## TEMEL BİLİMLERİN TEKSTİL VE MODA ÜZERİNE İZDÜŞÜMÜ: NANO-TEKNOLOJİ VE ŞARJ EDİLEBİLİR KUMAŞ ÖRNEĞİ

**ÖZET:** Bu çalışma, araştırma grubumuzun teknik tekstile olan çok-disiplinli yaklaşımını, elektriksel olarak doldurulabilir kumaş geliştirme proje örneği üzerinden sunacak ve projenin son durumunu, verilerle destekleyerek aktaracaktır. Bahsi geçen proje grafen nano-yüzey üretimi, tekstil kumaşını oluşturan elyafın grafen nano-yüzeyler ile kaplanması ve bunların üzerinde manganez elementinin oksitlerinin büyütülmesi ile uygun bir elektrolit içinde elektrot malzemesi olarak kullanılması fikrine dayalı olarak kurgulanmıştır. Bu çalışma, grafen nano-yüzey üretimi ve karakterizasyonu, kumaşa uygulanması ve kumaşın yüzey iletkenliğinin ölçülmesi, üstün-sığa mimarisinin oluşturulması ve elektro-kimyasal karakterizasyon ile sığanın ölçülmesi ayrıntılarını aktaracaktır.

**Anahtar Kelimeler:** Nano-teknoloji, grafen, üstün-sığa, giyilebilir teknoloji, depolama, batarya

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DOI: 10.7216/130075992015229704, [www.tekstilvemuhendis.org.tr](http://www.tekstilvemuhendis.org.tr)

## 1. INTRODUCTION

Physico-chemical properties of materials start to deviate from those when they are in bulk form, given the components forming them shrink to smaller sizes. Shrinkage in size, benefiting from higher surface area of materials, or in other words a larger ratio of surface-to-volume, leads to manifestation of some new features which otherwise either do not exist or are there but negligible in bulk. The dimensions at which these new features start to dominate over those in bulk, corresponding fabrication and characterization methods with a vast variety of application techniques are all together considered to form an emerging multi-disciplinary field of nano-science. Application areas of nano-science in technical textiles -at the time of this writing- are widening and keep a significant number of research groups busy world-wide.

When decorated with nano-structures, fibres forming the textile materials -in addition to their conventional qualities- start to exhibit new and innovative features which are not achievable through conventional techniques involved in textile manufacturing. These textile fabrics having new surface features allow producers to apply new production methods to achieve an unprecedented spectrum of material science applications in textile form. Such innovative materials find application areas in technical textiles [1] such as energy harvesting and storage [2, 3].

It is reported in the literature [4, 5] that fibers forming a textile fabric can be conformally coated with a single atom thick nano-sheets of carbon, called graphene, geometrically isolating the surface of the fibers from their surroundings. Upon graphene coating of fibers, molecules and/or other nano-structures, which normally cannot be bound to conventional textile materials, can then be attached or grown on each of the fibers. Graphene coating does not only function as a substrate for other additives but also makes the fabric electrically conductive. Fabric conductance, coupled with the availability of growing pseudo-capacitive nano-crystals such as manganese-oxides, suggests that the fabric can function as an electrode material within a suitable electrolyte, forming a charge-able battery [6] in textile form just as good as any other battery.

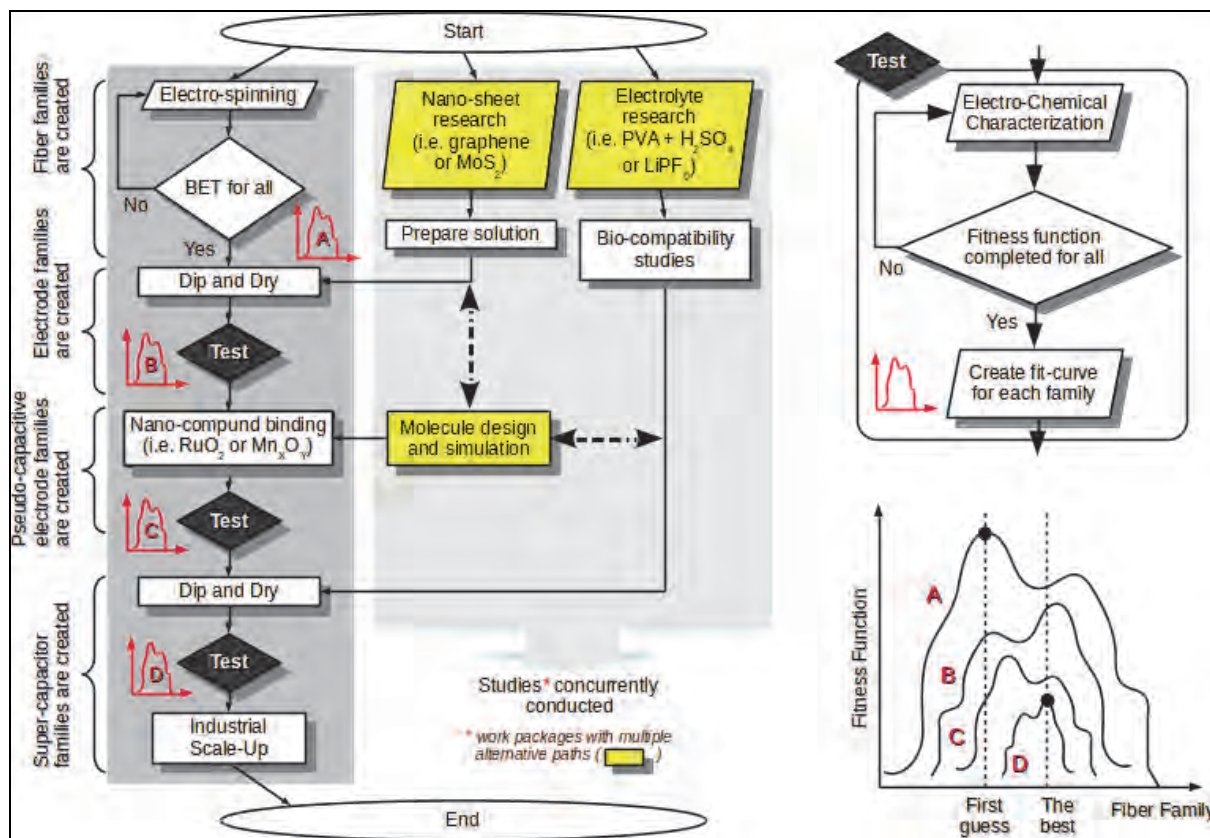
Super-capacitors (SC), formerly named as electric double-layer capacitor (EDLC) or ultracapacitor, is the generic term for a family of electrochemical capacitors which don't have a conventional solid dielectric. The capacitance of an electrochemical capacitor is determined by two storage principles, which both contribute indivisibly to the total capacitance: i) *double-layer capacitance* which is the electrostatic storage achieved by separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte where the separation of charge is of the order of a few Ångströms (i.e. 0.3 – 0.8 nm), that is, much smaller than in a conventional capacitor and ii) *pseudocapitance* which is the Faradaic electrochemical storage with electron charge-transfer, achieved by redox reactions, intercalation or electro-sorption.

Capacitors and batteries fundamentally differ in terms of the amount of charge they can hold (i.e. energy density) and the rate at which they can deliver power to external circuitry (i.e. power density). Batteries usually have higher energy densities but are not capable of delivering high power levels, whereas capacitors usually cannot store large amounts of charge, however, can deliver large power levels. SCs are transitional in-between batteries and capacitors in that they can store larger amounts of charge -in other words higher energy densities- compared to capacitors and deliver larger levels of power -or higher power densities- compared to batteries, trying to benefit from and/or join together both worlds. The amount of charge an SC can hold mainly depends on the effective surface area of the electrode materials and the number of parallel redox reactions taking place at the electrode-electrolyte interface.

## 2. METHODOLOGY

Considering the scope of this manuscript, we will intentionally exclude many actually-inevitable discussions on the specifications related to power electronics in order to realize a real-world SC and focus only on textile application.

Project flow is summarized in Fig.1 conceptually and strictly followed throughout the conduction of the experiments. We start with fabric material selection



**Figure 1** - Flow chart of the project. Dark frame represents the main flow with parallel work packages (yellow, lighter frame). At the end of each step, a fitness function is calculated (bottom-right plot) as a function of material (fiber family)

and construction followed by nano-sheet application which has a function in crystal growth similar to mordanting in conventional dyeing. Pseudo-capacitive nano-crystals growth and electrode characterization by electro-chemistry finalizes the project. Note that each and every project step has the potential to change the direction of the project as any fittest condition out of a certain step can be falsified by the next, represented by the peak locations of the curves A, B, C, and D. Just as an example, higher surface area does not necessarily lead to higher capacitance values as the penetrability of the electrolyte might be limited for small pore sizes. In other words, even though, finer porosity of the base fabric results in larger effective area, potentially allowing a higher number of parallel red-ox interactions, unnecessarily small pores decrease the accessibility of the nano-coating, pseudo-capacitive compounds and the electrolyte, respectively, lowering the performance of the final device which is measured in a later stage. The subject requires multi-disciplinary activities within the framework of nano

material science in general and has strong bases particularly on chemistry, physics, and engineering disciplines. The main objective is to build an electrically chargeable textile fabric in large scale, suitable for being seamlessly embedded into garments for powering up mobile devices. Components of the main objective are described in the following subsections.

### 2.1. Designing the Base Fabric

A set of highly porous natural and/or synthetic materials, providing the individual fibers as the electro-chemical interaction zones, should be decided at the very beginning. These may range from natural cellulose to electro-spun porous polymers. Porosity of the base material is one of the key variables to optimize because it decreases the number of parallel red-ox interactions at both of the extremes. BET surface area and porosity analysis, and electron-microscopy are expected to give a ranking between different choices.



## 2.2. Synthesis of Graphene Suspension

Depending on the conductance of the base fabric, in order to decrease the resistance and/or to establish a base coating on which other nano-structures can be grown or chemically bound, a thin layer of elements or molecules could be needed. Raman/FTIR spectroscopy, XRD and electron-microscopy would point out the best coating in case such an additional layer is needed [7-11].

## 2.3. Converting the Base Fabric into an Electrode

Individual fibers of nominally non-conductive base fabric, establishing the dominated physical properties, is coated with nano-sheets of conductive elements such as but not limited to graphene [12-18]. This is expected to be a thin conformal coating which makes the fibers conductive without affecting their physical properties significantly. It is analogous to mordanting in dyeing process.

## 2.4. Choice of Electrolyte and Production of the Final Device

Electrolyte, as an electronically non-conductive ion transfer medium, hosts the electrodes within its volume. In addition to its electronic performance as electrolyte material and its mechanical properties that would have significant effects on how well it penetrates into the porous electrode material, the choice of material should also consider biocompatibility as this material might form the outermost layer of the final device. Following the laboratory-scale optimization and tests of all the components, comes the process of placing things in place to fabricate a large-scale version of the finished fabric ready for final as-device characterization.

## 2.5. State-of-the-art

Nano-structures such as but not limited to pseudocapacitive crystals grown on functionalized graphene nano-sheets, which in turn coat the individual fiber surfaces forming the actual fabric, have been demonstrated to be successful candidates for high performance SCs [11, 16-18]. However, these studies -brilliant and promising though they are- hardly reach 10% of the theoretical expectation (e.g. ~150 F/g

compared to 1300 F/g for the oxide of Mn) for specific capacitance values which is in units of Farad per mass of the nano-structure utilized. This is mainly due to the limited number of pseudo-capacitive nano-structures reachable electronically. Additionally, the limitation is contributed by the fact that the interface between electrolyte and the nano-compounds is not as high as the theoretical expectation. As an example, the theoretical surface area of graphene is ~2700 m<sup>2</sup>/g of which only a fraction is accessible [13, 14]. These suggest that, in addition to the choice of different materials, there is room for an order of magnitude improvement in terms of achievable capacitance. One can hope to converge to the expected maximum as much as possible via optimizing nano-structure synthesis to address the above issues. Optimizing the porosity of the base fabric increases the effective interface in-between the nano-compounds and the electrolyte. Additionally other nano-compounds which can encounter multiple redox reactions may also be investigated.

Besides the electrode material, choice of the electrolyte plays an important role both electrochemically and mechanically. Studies published in the literature usually utilize toxic liquid electrolytes which renders the final devices non-suitable for textile. One would like to develop a suitable gel electrolyte which is non-toxic and is bio-compatible, without the loss of electro-chemical performance. It is logical trying to develop methods to either isolate the toxic part and/or to develop a hazard-free material by itself as the electrolyte. Considering human skin contact, besides the electro-chemical function, a non-allergic behavior and non-cytotoxicity are the main targets as well.

In addition to the above issues, the published literature usually attacks a specific problem and addresses the issues thoroughly, however, leaving other issues, which are connected directly or indirectly, almost untouched. This cannot be emphasized more, especially in textile. Among these cost, industrial scaling, and actual device design issues can be counted. Moreover, biocompatibility, body comfort and battery function as the basic expectations from such fabrics are at least treated as conflicting and usually not addressed concurrently.

One hopes to address all the issues within a big picture concurrently and develop an industry-compatible production process.

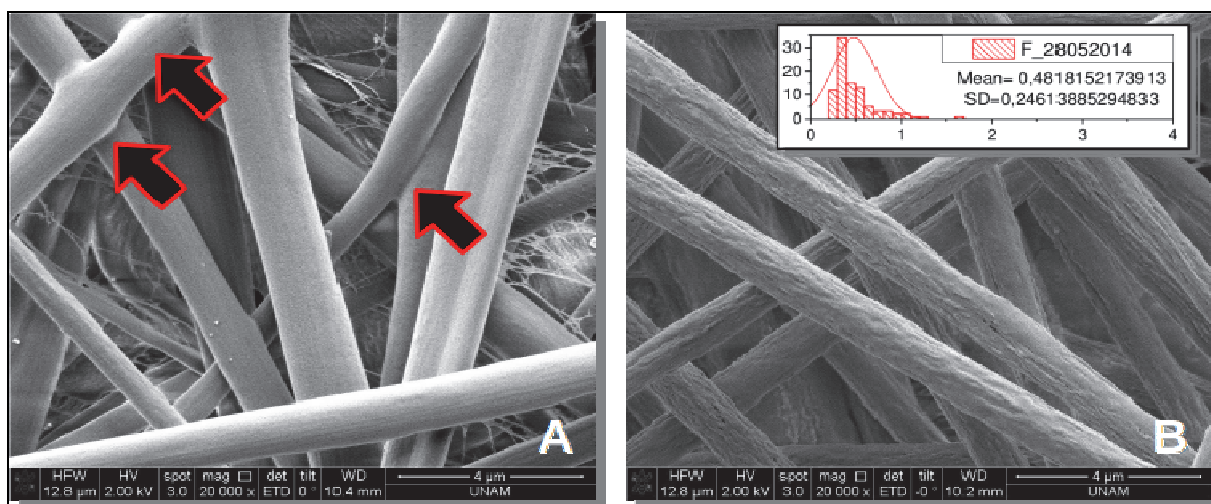
### 3. RESULTS AND DISCUSSION

Next sections will summarize nano-fibre and nano-sheet production and characterization methods as well as application to textile and characterization in the form of textile.

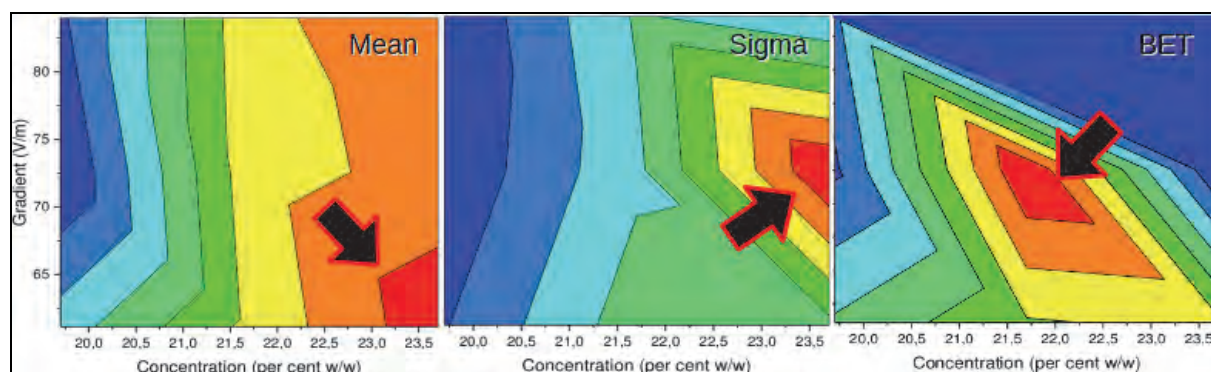
#### 3.1. Fabrication of Base Fabric

Electro-spun thermo-plastics provide high surface-area-to-mass ratios, increasing potentially the number of concurrent redox reactions, which are the basic

interactions taking place in a battery. They are also very light compared to many other conventional textile materials such as cotton. However, the process is usually a strong function of many parameters, which need to be controlled, in manners of negative feedback. Fig. 2 shows our very first experiments to produce electro-spun thermoplastic materials with very high surface areas. Fabrication conditions play a significant role; Fig 2.-left shows joint fibres (marked with arrows) as a result of non-optimum running conditions, decreasing available surface area as well as worsening the physical properties. The material in this case tends towards behaving like a layer with no breathability instead of exhibiting textile-like features.



**Figure 2.** SEM images of thermoplastic nano-fibers electro-spun under non-optimized (left) and optimized conditions. Arrows point conjunctions between fibers, an undesired feature. Inlined plot is the fiber diameter distribution histogram.



**Figure 3.** Statistical characteristics of fiber diameter distribution vs experimental conditions (left, middle) and surface area as a function of the same. Note the non-coherence

Coherent with the expectation represented in Fig.1, Fig.3 shows an interesting mismatch in requirements for optimal experimental conditions. The mean of fiber diameters suggests that the electric field gradient should be as high as possible and the solution concentration should be as low as possible for minimum fiber diameter. Standard deviation of the fiber diameter does not fall apart and follow the same trend suggested by the mean fiber diameter. However, the surface area measurements showed an unexpected trend as the optimum condition is somewhere in the middle for both the variables, gradient and concentration. This mismatch can be interpreted in a few different ways: one convincing explanation is that the gas molecules used for the BET measurements get adsorbed on the fibers of the cooled down sample, close to the surface first, functioning as catalytic surfaces for the newcoming gas molecules, which in turn keep being adsorbed more and finally blocking the passage to inner pores. Since the fabric material is close to be effectively 2-dimensional, gas molecules used for calculation of pressure drop cannot find alternative paths to penetrate deep into the material, leading to errorous measurement results. In such cases, material can be cut down in small pieces, however, this has other disadvantages such as the effect of increased surface area just by the act of cutting.

In addition to electro-spinning, ordinary cotton woven fabrics with surface areas of the order of a few tens of meter squares are also used for the experiments. They have the advantage of mechanical stability over electro-spun non-wovens, however, lack huge surface areas intrinsically associated to nano-fibers. Non-textile surfaces are also considered, however, they are even worse than woven ordinary fabrics as the effective surface area is equal to the geometric area of the sheets.

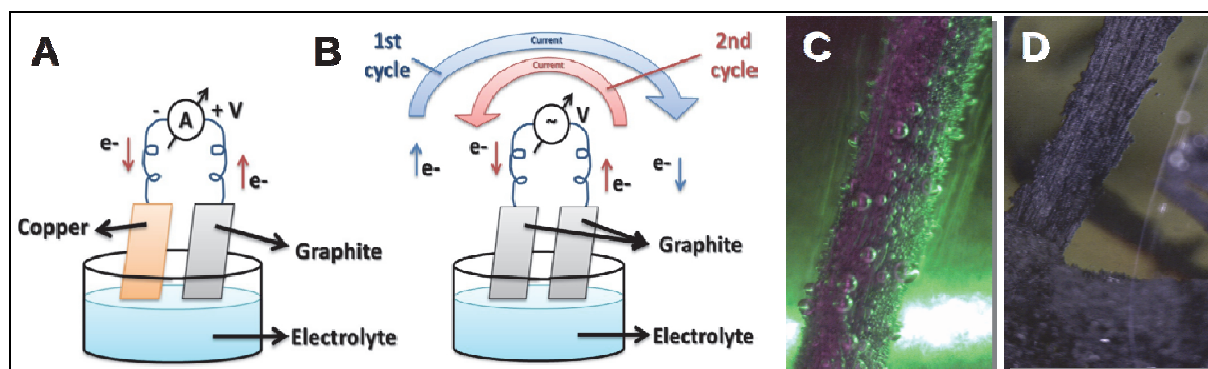
### 3.2. Graphene Nano-Sheet Fabrication

Since the first characterization of graphene in 2004 [13], different methods for graphene production under

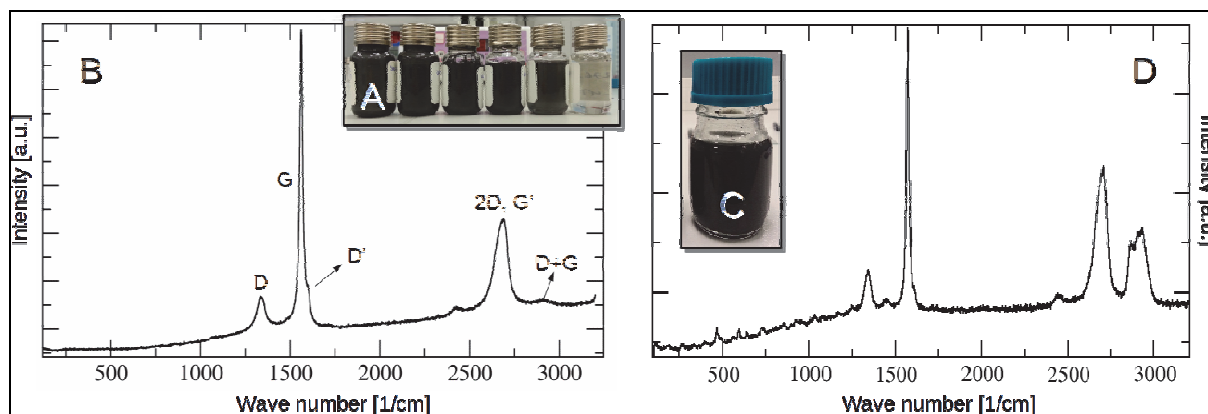
the following two main ideas are proposed with varying yields and target applications. The two basic approaches are to cleave multi-layer graphite into single layers and to grow it epitaxially by depositing one layer of carbon onto another material. Among others, mechanical and electro-chemical exfoliations of solid graphite electrodes are considered to be the fittest two for textile application. This is because these two aqueous exfoliation methods do not require harsh chemical processes, which are harder to control, such as Hummer's method [22] and its derivatives.

Fig. 4 shows the two basic arrangements for graphite exfoliation into pristine and/or functionalized graphene nano-sheets. The set-up shown in Fig.4-A is used to exfoliate graphite rod into sulphonated graphene nano-sheets via deposition of  $\text{SO}_4^{2-}$  ions from the sulphuric acid of the electrolyte on and in-between graphene layers, a process called "intercalation". Intercalated layers leave the graphite electrode and are either suspended within the electrolyte or precipitate at the bottom of the reactor. The arrangement of Fig.4-B moves the idea a step forward by replacing the metal electrode, which does nothing but provides the current, with yet another graphite electrode and at the same time by using an alternating bias instead of DC. This method obviates the need for a metal electrode with very high corrosion resistance and more importantly doubles the rate of exfoliation process. The yield is higher as both the electrodes decay into graphene nano-sheets concurrently due to the fact that oxidation (i.e. exfoliation) and reduction (i.e. removal of sulphonated groups from partially exfoliated graphene layers) take place concurrently and alternately at the opposite electrodes. This means that the duty cycle of the biasing potential difference at the graphite electrodes is fully utilized as opposed to techniques utilizing metal (e.g. copper, platinum) counter electrode and cyclic voltammetry. Fig.4-C shows one graphite electrode at the very beginning of the process; the bubbles are formed due to  $\text{H}_2$  gas release. Partially exfoliated/corroded graphite rod and precipitated material are shown in Fig.4-D.





**Figure 4.** Electro-chemical exfoliation of graphite rods into graphene nano-sheets within aqueous sulphuric acid solution. A: DC powered exfoliation of sulphonated graphene, B: double-graphite cyclic exfoliation, C: graphite electrode under electrical bias, D: partially exfoliated electrode and precipitation.



**Figure 5.** Graphene suspensions and corresponding Raman spectra. A is the set of sulphonated graphene dispersions, B is the Raman spectrum in solid state with characteristic peaks denoted, C is the dispersion of mechanically grinded/exfoliated graphite, and D is its Raman spectrum in solid state.

Graphene sheets are suspended via utilization of a suitable surfactant formulation after or even during the electro-chemical exfoliation process. Fig.5-A shows such a suspension and its consecutive 8x dilutions representing the very high density of the nano-sheets together with nano-particles which are inevitable in such a process. In order to separate aggregates, graphite particles, and graphene nano-sheets with higher number of layers from high quality graphene material, a cyclic application of centrifuge to precipitate, addition of washing solution and sonication to re-disperse the material is applied several times. Vacuum filtration is not used as filter pores are susceptible of letting go of the highest quality graphene sheets due to size.

### 3.3. Characterization of Exfoliated Nano-Sheets

Suspensions are characterized mainly by Raman spectroscopy, dynamic light scattering, and atomic force microscopy.

DLS is by definition not sensitive to high quality graphene nano-sheets as light passes through graphene layers without much absorption and DLS counts only on opaque nano-particles and aggregates as the technique depends on diffraction pattern of light through the liquid sample. Therefore, DLS technique is used for characterizing the precipitated material separated from those used for spectroscopy. DLS showed a single peak at a few hundreds of nano meters to tens of micro meters, representing larger exfoliations not to be used for graphene coating.



AFM is used to confirm nano-sheet thickness on a glass sample holder. Depending on what functional group is attached onto the nano-sheets, thickness varied accordingly. However, AFM study can not reflect statistical significance as it depends only on a few selected samples (out of millions) properly separated from their environment. Therefore, its use is intrinsically limited to isolated flakes of individual nano-sheets.

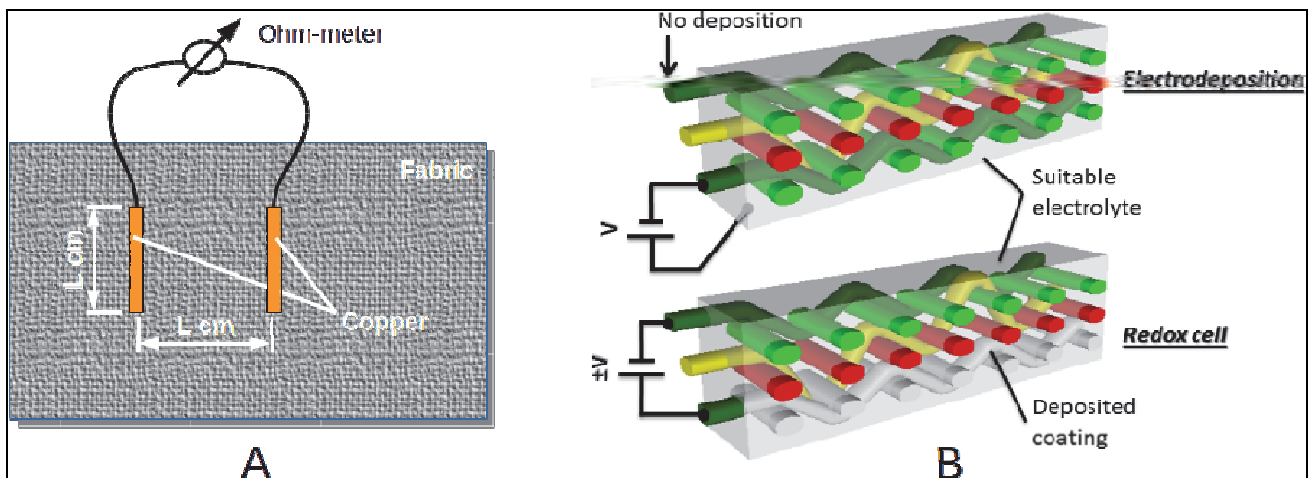
Fig.5-B shows a solid-state Raman spectrum of sulphonated graphene produced by the arrangement depicted in Fig.4-A, with copper as counter electrode, aqueous  $H_2SO_4$  and KOH solution as electrolyte under DC bias. Characteristic bands are also depicted. D band in the spectrum represents C-CH<sub>3</sub> bonds (display for peripheral length of the nano-sheets) and G band is for C-C and C=C bonds (display for nano-sheet area), whereas decomposability of 2D or G' band into more than one fixed-width Lorentzian is due to multiple layers. Fig.5-C is the mechanically exfoliated and/or grinded graphite powder and D is its corresponding Raman spectrum. Intensity ratio of D and G bands,  $I_D/I_G$ , together with the number of decomposing peaks forming 2D band are representation of the quality of the graphene nano-sheets [9, 10]. Despite similarities, note that the two techniques produce different graphene geometries as well as surface chemistries.

### 3.4. Application and Characterization in Textile Form

Upon preparation of graphene suspensions, ready-for-dyeing stage fabrics are dipped into the dispersion and dried within an oven at 50°C. The application can be repeated in order to increase material deposition and enhance the coating thickness. Fabrics after the application, turn their colour gradually to black and their surface resistance gradually drops with the amount of deposition.

Surface resistance of the fabrics are measured using two metal conductors of equal length placed a distance equal to their length apart and pressed moderately (~1 kPa) as depicted in Fig.6-A. An ordinary ohm-meter is then utilized to measure the electrical resistance between metals in units of ohm/sq. The measurements showed that the approximated surface resistances of the graphene-coated fabrics range from a few ohm/sq. to a few hundreds of ohm/sq., low enough for the fabric to be used as an electrode and even as current collector within a redox cell.

After characterization of surface resistance of the graphene-applied fabrics, solution-based coating or electro-deposition of manganese oxides (i.e.  $Mn_xO_y$ ) becomes possible. Fig.6-B depicts the repeating unit for a three-layer fabric construction where green colour represents graphene coated conductive yarns forming pseudo-electrode layers. These are separated



**Figure 6.** Surface resistance measurement set-up (A) and selective nano-crystal growth arrangement for a multi-layer fabric by means of electro-deposition.

by the red isolating yarns forming an isolating pseudo-layer and all three pseudo-layers are interconnected by the yellow binder yarn having no electronic features. This arrangement allows one to selectively conduct electro-chemistry on one conductive pseudo-layer to grow oxides of manganese. As shown in Fig.6-B-top, bottom pseudo-layer is connected within an electro-deposition circuit, leaving the other pseudo-electrode intact. Manganese oxide coating - represented as white coating in the bottom figure-differentiates the two pseudo-electrodes, creating a redox cell arrangement. This arrangement is now suitable to be used as a battery fabric within a suitable electrolyte as depicted in Fig.6-B-bottom. However, the same SC geometry can also be achieved by fabricating two electrode materials by utilizing 2D woven fabrics with ordinary constructions and stacking them on top of each other. This obviates the need for a 3D weaving infrastructure.

Cyclic voltammetry (CV) and electro-chemical impedance spectroscopy (EIS) are the two main techniques to characterize capacitors and batteries as well as an SC. The basic principle of these techniques is to sweep a certain potential difference range back and forth across the electrodes and concurrently monitor the amount of current through the device as a function of bias switching frequency. Actually complex in nature, these techniques mainly count how many electrons the device-under-test (DUT) can host and then deliver to an external circuitry in a cyclic manner in order to measure its capacitance in units of Farads or mA hours.

#### 4. CONCLUSIONS

A battery construction in multi-layer textile fabric form is presented. Decision criteria for material selection and production method of base fabric as well as characterization methodologies are described. Electro-spinning of thermoplastics is followed as an example for base fabric production. A detailed discussion of fibre diameter distribution as a function of experimental variables, and experimental issues of surface area and porosity analysis of 2D materials is provided. Graphene nano-sheet fabrication pathways, which are considered suitable for application in textile, are summarized and two new facile methods are introduced with corresponding spectroscopic analysis techniques for quality assessment. Textile

application of graphene, which functions as substrate for growth of pseudo-capacitive manganese nanocrystals, and surface resistance characterization of graphene-coated fabrics are shown. Techniques from electro-chemistry for super-capacitor characterization are also described.

#### ACKNOWLEDGMENTS

The authors would like to thank: Özgür Akdemir for preparation of solutions used for the electro-spinning experiments, Deniz Şener for conducting the very first electro-spinning experiments, Nejdiye Güneş for laboratory work of electro-chemical exfoliation, and the last but not the least Agamirze Hamitbeyli for invaluable discussions on fundamentals of chemistry.

This work is partially supported by the TÜBİTAK under TEYDEB-3130738.

#### REFERENCES

1. Lukowics, P., Kirstein, T., Tröster, G., (2004), *Wearable Systems for Health Care Applications*, Schattauer Publishers, Methods Archive, vol.43, no.3, pp.232,238.
2. Bonderover, E., Wagner, S., (2004), *A woven inverter circuit for e-textile applications*, Electron Device Letters, IEEE, vol.25, no.5, pp.295,297.
3. Gualous, H., Louahlia-Gualous, H., Gallay, R., Miraoui, A., (2009), *Supercapacitor Thermal Modeling and Characterization in Transient State for Industrial Applications*, Industry Applications, IEEE Transactions on, vol.45, no.3, pp.1035,1044.
4. Hu, L., Chen, W., et al., (2011), *Symmetrical MnO<sub>2</sub>-Carbon Nanotube-Textile Nanostructures for Wearable Pseudocapacitors with High Mass Loading*, ACS Nano, 5 (11), 8904-8913.
5. Pasta, M., La Mantia, F., Hu, L., Deshazer, H., Cui, Y., (2010), *Aqueous supercapacitors on conductive cotton*, Nano Research, vol.3, no.6, pp.452,458, 10.1007/s12274-010-0006-8.
6. Chen, S., Zhu, J., Wu, X., Han, Q., Wang, X., (2010), *Graphene Oxide-MnO<sub>2</sub> Nanocomposites for Supercapacitors*, ACS Nano, 4 (5), 2822-2830.
7. Coleman, J.N., et al., (2011), *Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials*, Science, vol.331, no.6017, pp.568,571.
8. Lotya, M., King, P., Khan, U., et al., (2010), *High-Concentration, Surfactant-Stabilized Graphene Dispersions*, ACS Nano, 4(6), 3155-3162.
9. Malard, L.M., Pimenta, M.A., et al., (2009), *Raman Spectroscopy in graphene*, Physics Reports, vol.473, pp. 51,87.

10. Ferrari, A.C., Meyer, J.C., et al., *Raman Spectrum of Graphene and Graphene Layers*, Physical Review Letters, vol.97, 187401.
11. Part, S., An. J., et al., *Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets*, ACS Chem. Mater., 20 (21), 6592-6594.
12. May, J.W., (1969), *Platinum surface LEED rings*, Surface Science, vol.17, 267-270.
13. Novoselov, K.S., Geim, A.K., et al., (2004), *Electric Field Effect in Atomically Thin Carbon Films*, Science, vol.306, no.5696, pp.666,669.
14. Zhu, Y., Murali, S., et al., (2010), *Graphene and Graphene Oxide: Synthesis, Properties, and Applications*, Advanced Materials, 10.1002/adma.201001068.
15. Wu, M., Snook, G.A., et al., (2004), *Redox deposition of manganese oxide on graphite for supercapacitors*, Electrochemistry Communications, 499-504.
16. Yu, G., Hu, L., et al., (2011), *Solution-Processed Graphene/MnO<sub>2</sub> Nanostructured Textiles for High-Performance Electrochemical Capacitors*, ACS Publications, vol.11, pp.2905,2911.
17. Chen, S., Zhu, J., Wu, X., Han, Q., Wang. X., (2010), *Graphene Oxide-MnO<sub>2</sub> Nanocomposites for Supercapacitors*, ACS Nano, 4 (5), 2822-2830
18. Winter, M., and Brodd, R.J., (2004), *What are Batteries, Fuel Cells, and Supercapacitors*, Chemical Reviews, 104 (10), pp.4245,4270.
19. Hummers, Jr., William, S., (1957), *Preparation of Grafitic Acit*, Patent, US 2.798.878.