

# MODIFIED MULTILAYER GRAPHENES FOR SUPERCAPACITORS

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## Introduction

Electrical double layer (EDL) capacitors are energy storage devices that bridge the gap between conventional capacitors and batteries in terms of power and energy density [1, 2]. With their fast charge/discharge rates and long life cycles, EDL capacitors (also known as supercapacitors/ultracapacitors) complement batteries for transportation (plug-in and hybrid vehicles) and grid applications [2, 3]. High surface area carbons are extensively and almost exclusively used as electrode materials in electrochemical capacitors for electrical energy storage [1, 2, 4]. Currently employed carbon materials meet most of the supercapacitor requirements in terms of power density, but have lower energy storage capacity than batteries. To increase the energy-power characteristics of supercapacitors, a breakthrough electrode material with large surface area and high electrical conductivity is needed.

Graphenes are mono-atomic layers of carbon atoms bonded in  $sp^2$  hybridization [5]. These remarkable carbon materials have a wide range of potential applications because of their unique properties, i.e. very high electrical ( $\sim 10^4 \Omega^{-1} \text{cm}^{-1}$ ) and thermal conductivity ( $5000 \text{ Wm}^{-1} \text{K}^{-1}$ ), large surface area (theoretically  $2630 \text{ m}^2/\text{g}$ ) and Young's modulus ( $1100 \text{ GPa}$ ) [6]. Graphenes are an ideal candidate material for supercapacitor applications because of their large surface area and high electrical conductivity. The large surface area of graphenes can help to store more charges at the electrode-electrolyte interface and hence increases the energy storage capacity. The high conductivity is crucial for the easy transportation of electrons from the electrode to the current collector with little resistive energy loss, which helps to better utilize the stored energy and improve the power of the device. The interest in graphene materials for supercapacitor applications has been gradually emerging. A couple of publications have reported on experimental works using reduced graphene materials for supercapacitor applications [7, 8]. In addition, there are a few research articles related to theoretical calculations or experimental works on graphene (graphite) oxide for supercapacitors.

In this project, we report on multilayer graphene materials synthesized using a high throughput technique and their morphological and structural characterization. The multilayer graphenes will be modified using a thermo-chemical method. These modifications are expected to enhance the energy storage of multilayer graphene-based supercapacitors due to

increased electrostatic (EDL) and faradic (pseudocapacitive) contribution.

## Experimental

Graphene materials were synthesized using high throughput technique [6], which is a colloidal chemistry method based on oxidation and exfoliation of graphite, followed by liquid phase reduction of graphite oxide. Initially, the graphite oxide was prepared through the oxidation of graphite powders using the modified Hummers method [9]. This method involves two stages of oxidation using first  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{P}_2\text{O}_5$  in acidic medium and later a strong oxidizing mixture for total oxidation. The prepared graphite oxide material was then separated and reduced using hydrazine. Through this method a large amount of single and multi-layered graphene materials were produced. The synthesized graphene materials were characterized using techniques such as XRD, SEM, and gas adsorption.

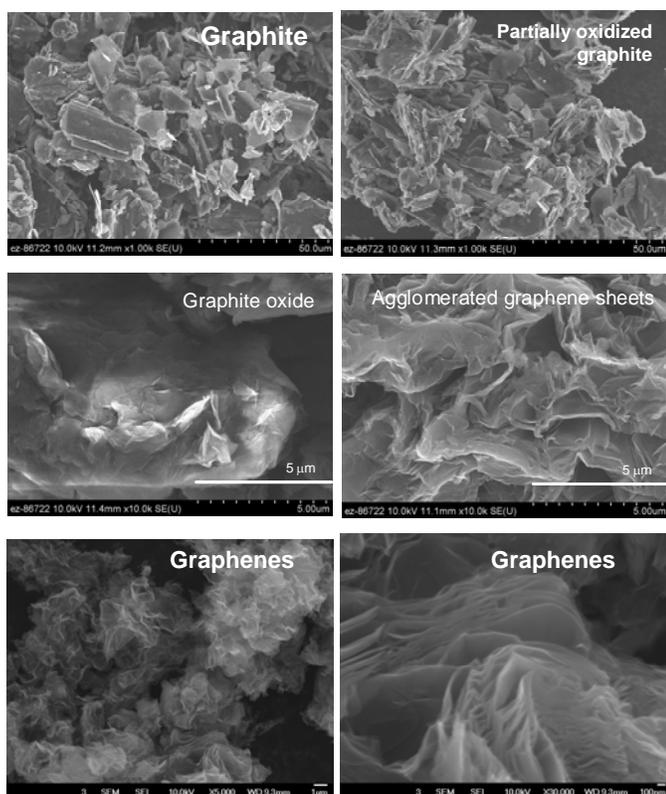
Graphene materials will be modified using a thermo-chemical method, in order to create holes, carve edges, and also introduce redox-active chemical groups on the graphene surface, and therefore enhance the energy storage capacity of graphene-based supercapacitors due to increased electrostatic (EDL) and faradic (pseudocapacitive) contribution. The electrochemical properties of selected materials will be characterized by applying standard techniques: the specific EDL capacitance and the added contribution of pseudo-capacitance will be measured in a three electrode cell assembly using cyclic voltammetry; the capacitance and time constants during positive and negative polarization will be measured using impedance spectroscopy. Depending on the properties of modified graphene materials, the best-performing samples will be selected, and their stability and self-discharge properties will be characterized using galvanostatic charge-discharge cycles in a two electrode configuration.

## Results and Discussion

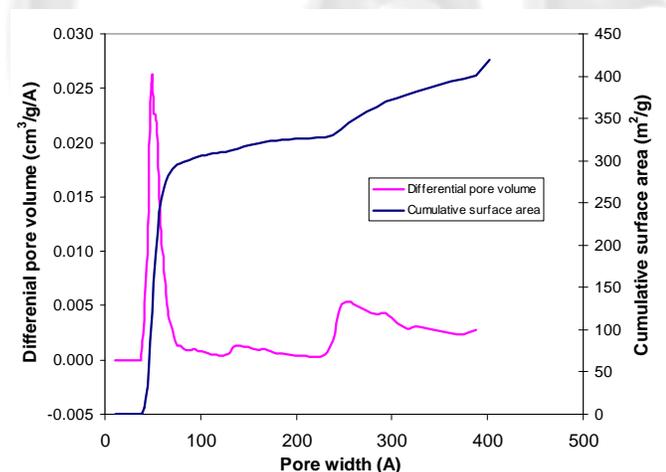
Figure 1 shows various SEM images taken at various stages of the synthesis process, The last two images shows graphenes at two magnifications (5,000X and 30,000X) detailing the overall texture of the synthesized graphene materials. The domains of several layers thick are observed on the highest magnification image.

The BET surface area of as-synthesized graphene materials is  $380 - 400 \text{ m}^2/\text{g}$ . From Figure 2 it is observed that the pore size distribution is bimodal with maxima in the range of  $4-6 \text{ nm}$  and  $25-40 \text{ nm}$ . About 75 % of BET surface area is comprised in narrow mesopores ( $< 8 \text{ nm}$ ).

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**Fig. 1** SEM images at various stages of the graphene synthesis process.

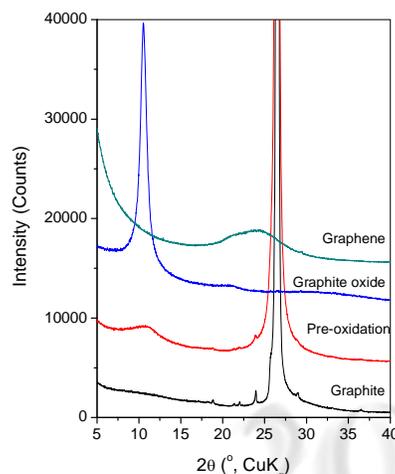


**Fig. 2** Cumulative surface area and differential pore volume of graphene materials.

Figure 3 shows the x-ray patterns at the various stages of the preparation process. The 002 peak is well defined in graphite precursor, then it shows that graphite is partially intercalated in pre-oxidation stage, and completed intercalated at the graphite oxide state. As graphenes, the peak position shifts to lower angles, indicating an increase in the separation of graphene layers.

## Conclusions

Graphene materials were successfully synthesized and characterized via BET surface area, x-ray diffraction, and electron microscopy. Thermo-chemical modification of graphenes is underway and we expect to report on the electrochemical properties of the as-synthesized and modified graphenes at the conference.



**Fig. 3** X-ray diffraction patterns at various stages of the process of preparation of graphenes.

**Acknowledgments.** Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. SEM and x-ray diffraction was performed at the Shared Research Equipment (SHaRE) user facility, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

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