

## Flexible Supercapacitors using Liquid Phase Exfoliated Graphene with Enhanced Specific Capacitance

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Graphene was synthesized by liquid phase exfoliation of graphite in DMF (N,N-Dimethylformamide) organic solvent. The synthesized graphene was characterized by TEM, SEM, UV-Visible and Raman spectrum. Graphene based paper electrodes were prepared by brush coating technique on A4 size paper. Four different gel electrolytes PVA/H<sub>2</sub>SO<sub>4</sub>, PVA/KNO<sub>3</sub>, PVA/KCL, PVA/KOH were used for making flexible supercapacitors and their characterization was done using cyclic voltammetry (CV) and galvanostatic charge / discharge (CD) curves. It was observed that PVA/KOH gel electrolyte exhibited maximum specific (Areal) capacitance of 30  $\mu\text{F}/\text{cm}^2$  which is greater than capacitance obtained from PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolyte.

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**Keywords:** Liquid phase exfoliation; Organic Solvent; Graphene based electrodes; Flexible supercapacitor; specific capacitance.

### 1. INTRODUCTION

Due to its extraordinary mechanical, electrical and optical properties graphene is the widely investigated nanomaterial for various electronics device applications[1]. Some of the excellent properties of graphene are its very high electrical conductivity, transparency and flexibility. These properties make graphene suitable for various applications like transparent displays, photovoltaic cells, OLEDs etc [2]. Graphene possess high specific surface area higher than activated carbons, which makes it a suitable electrode material for flexible supercapacitor [3]. Graphene has been synthesized by various methods such as mechanical exfoliation, chemical vapor deposition (CVD), Hummer's method and Liquid Phase Exfoliation method. Amongst these graphene synthesis method, Hummer's method is most widely used in which graphite is first converted into graphite oxide (GO)

by oxidation. Then graphite oxide (GO) is reduced into rGO (reduced graphene oxide) using various reducing agents like hydrazine hydrate, sodium borohydride etc. The as prepared rGO has many structural defects and impurities [4-6]. Due to these defects and impurities this method is not suitable for the synthesis of pristine graphene. Because of various harmful chemicals used, Hummer's method is not very safe for the synthesis of graphene.

There is a need of much safer method of graphene synthesis which can produce good quality graphene without the use of harmful chemicals. A much safer method is liquid phase exfoliation method in which the graphene is synthesized by exfoliating graphite directly in various organic solvents using sonication [7, 8]. This method is facile, safe, economical and less time consuming. For liquid phase exfoliation solvents such as Benzene, Toluene and Nitrobenzene, N-methyl-2-pyrrolidone (NMP) [9-11] have been utilized. Among these NMP has been found to give the maximum concentration of graphene. N,N-Dimethylformamide (DMF) is another organic solvent with surface tension close to NMP. In this work, DMF was used as solvent for graphene synthesis. Application of graphene as flexible supercapacitor has been explored by making conducting electrodes using brush coating method. The performance of the flexible supercapacitor depends upon the gel electrolyte sandwiched between the electrodes.

Gel electrolytes are prepared by mixing electrically conductive compounds in water with a polymer matrix such as polyvinyl alcohol (PVA). It has been reported that amongst the various acid, base, or salt-PVA gel electrolytes, the  $H_3PO_4$ -PVA electrolyte exhibited maximum specific capacitance with the graphene based electrodes [12]. It is known facts that a high ion concentration in the gel electrolyte can improve the capacitance. Therefore, here four different gel electrolytes PVA/ $H_2SO_4$ , PVA/ $KNO_3$ , PVA/KCL, PVA/KOH were investigated for the fabrication of graphene based flexible supercapacitors and their performances were analyzed using cyclic voltammetry (CV) and galvanostatic charge / discharge (CD) curves.

## 2. MATERIALS AND METHODS

### 2.1 Materials Used

Graphite extra fine powder, DMF (N,N-Dimethylformamide), Poly Vinyl alcohol, sulfuric acid, potassium nitrate, potassium hydroxide, potassium chloride were obtained from S. D. Fine chemicals Limited, Mumbai, India. All the chemicals were used as received, without any modification or purification.

### 2.2 Methods

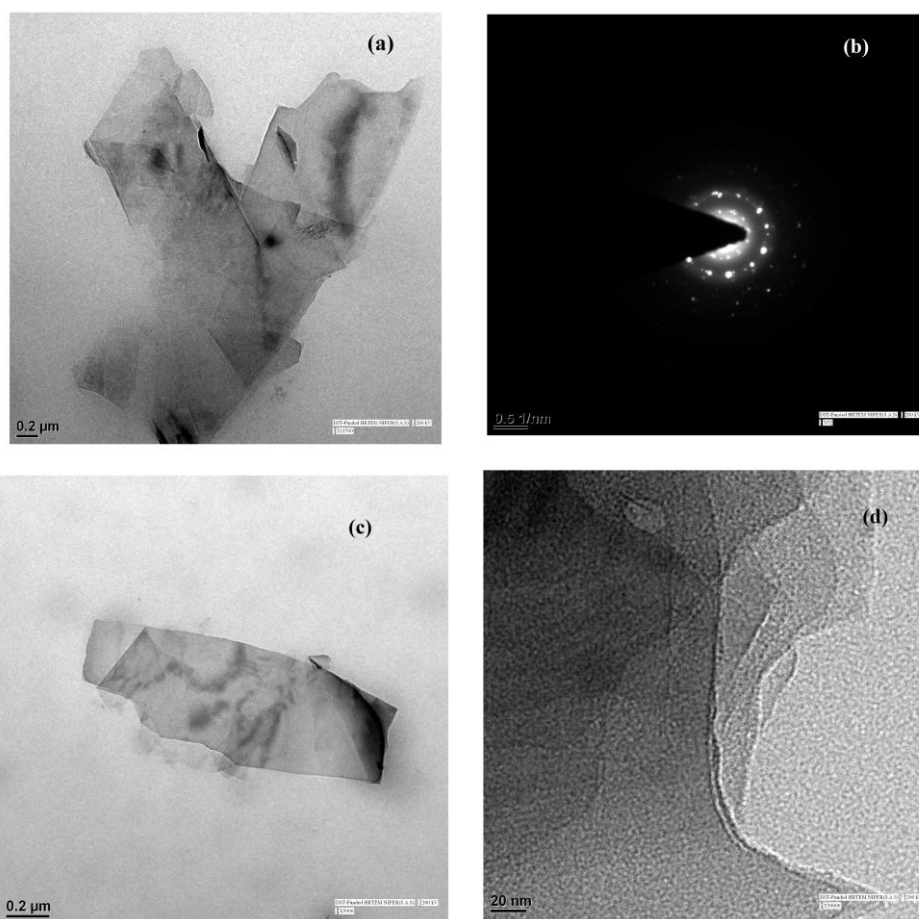
Graphene was synthesized by sonicating graphite powder (2g) in 300 ml of NMP solution using water bath sonicator (33 KHz, 500 W) for 9 hours. The obtained graphene dispersion was centrifuged at 3500 r.p.m. for 30 min. The intercalation of molecules on the graphene layers surface enhances the exfoliation as a result of sonication process. As the sonication time increases the

individual graphene nanosheets get exfoliated and synthesis of graphene from graphite source is completed. After the graphene synthesis, graphene dispersion was used for making electrodes using brush coating on A4 size paper.

### 2.3 Apparatus

The structural characterization of as synthesized material was done using transmission electron microscopy (FEI, TECNAI G<sup>2</sup>F-20) and micro structural analysis by scanning electron microscopy (Hitachi, S3400N) and graphene bond structure by UV-Vis spectroscopy with UV-VIS-NIR Spectrophotometer - Lambda 750 from Perkin Elmer, USA. Further to confirm the graphene formation and measure the quality, Raman spectrum was recorded and analysed using 785 nm laser. The electrochemical measurements such as cyclic voltammetry and galvanostatic charge discharge curves were plotted using inhouse AUTOLAB PGSTAT302N software facility.

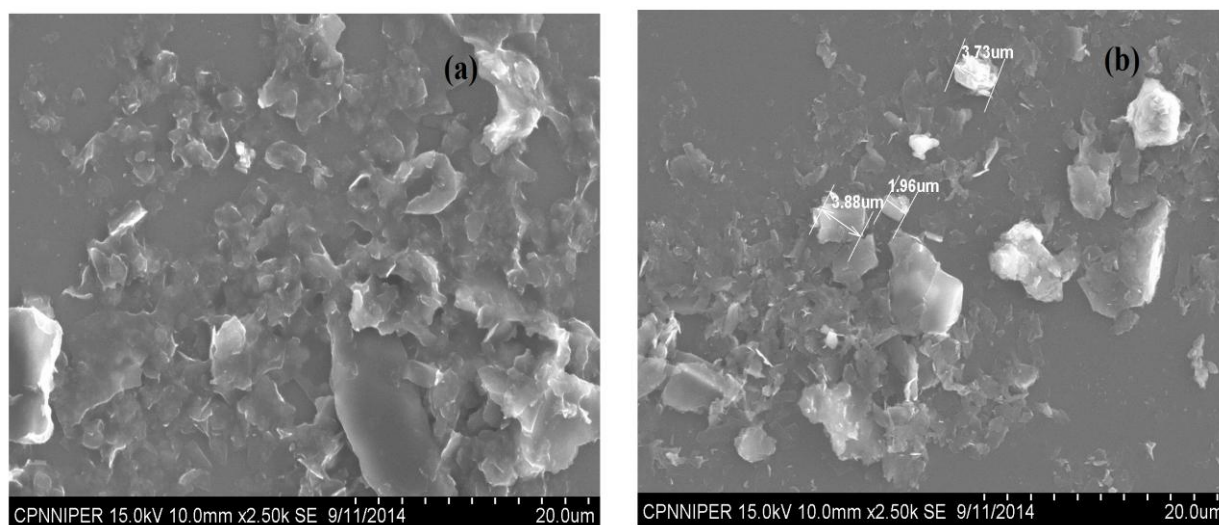
## 3. RESULTS AND DISCUSSIONS



**Figure 1.** TEM results of graphene nanosheets produced by liquid phase exfoliation of graphite in NMP solvent. (a), (b) shows single and multilayered graphene sheets, (c) shows the SAED pattern (d) shows overlapped graphene sheets.

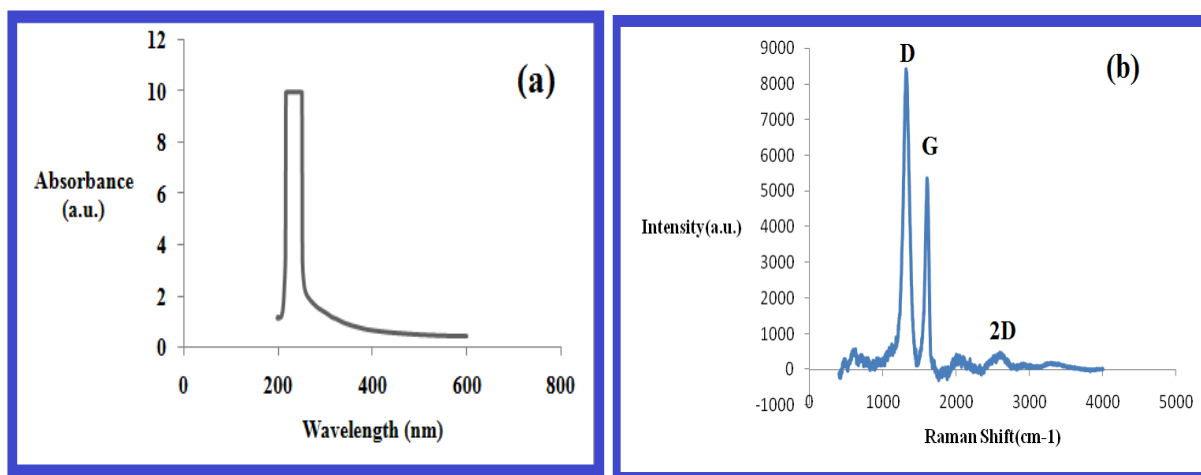
Graphene dispersion was characterized by TEM and SEM for determination of the structure and morphology of the graphene nanosheets. Characteristics UV–Vis absorption spectra of graphene dispersions were recorded between 200nm to 600 nm to find the wavelength corresponding to maximum absorbance value. Transmission electron microscopy (TEM) results show that the graphene dispersion contains graphene nanosheets of different lateral sizes ranging from few hundred nanometers to one micrometer as shown in the figure 1. A large number of multi layered graphene sheets overlapped one over one another. Fig 1(a) shows multilayered graphene nanosheet of 1500 nm lateral size . Fig 1(c) and Fig 1(d) shows single graphene nanosheet and overlapped graphene nanosheet of approx. 1 $\mu$ m lateral size. Fig.1 (b) shows the SAED pattern of the graphene sheet showing the hexagonal arrangement of atoms.

The scanning electron microscopy (SEM) images of the recorded samples is shown in Fig. 2. The image shown in Fig.2 (a) confirms the formation of multiple nanosheets of graphene produced as a result of liquid phase exfoliation of graphite in DMF solvent. From Fig.2(b) we observe that the graphene nanosheets have the lateral size of 785 nm ,986 nm ,1.25  $\mu$ m as shown in the diagram.



**Figure 2.** SEM results of graphene nanosheets produced by liquid phase exfoliation of graphite in NMP solvent.(a),(b) shows SEM results at different magnification

Further, the results obtained in TEM analysis indicates that as synthesized graphene possesses multilayered sheets corresponding to the  $p-p^*$  transitions of aromatic CAC bonds were also confirmed by UV-Visible spectrum of graphene in NMP solvent as shown in Fig.3(a). It has been reported in the literature that single and multi-layered graphene nanosheets produce UV–vis absorption peak near 265 nm due to the  $p-p^*$  transitions of aromatic CAC bonds[12].The peak absorbance of graphene oxide occurs at 223 nm.In the present study, the absorption peak is observed shifted towards 223 nm ,i.e. at lower wavelength because of graphene oxide defects present in the graphene, as also evident from the raman spectrum as shown in Fig.3(b).The flat top peak as compared to round peak at absorbance 10 a.u. is because of the high graphene concentration in the sample used for UV-Vis characterization.

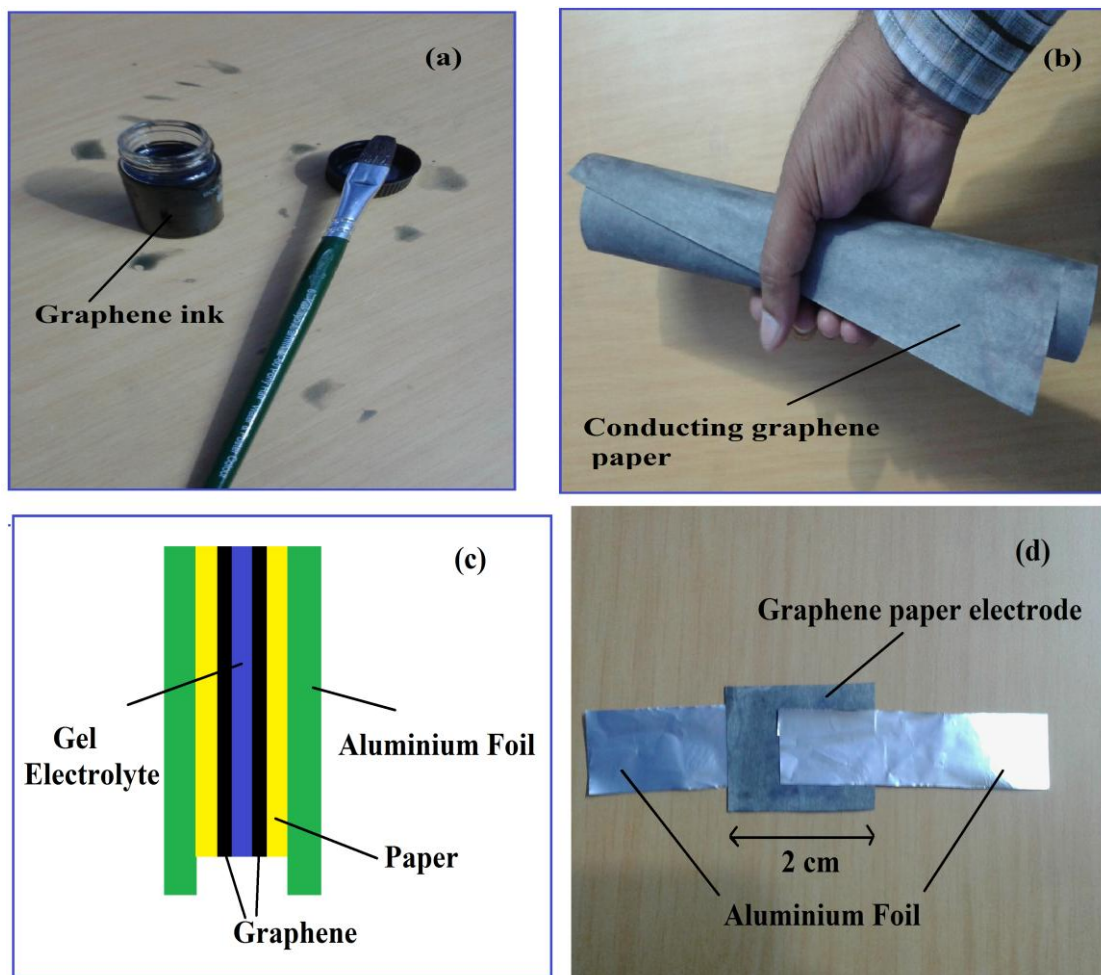


**Figure 3.**(a) UV-Visible spectrum of graphene ink in NMP solvent.(b) Raman spectrum of Graphene nanosheets showing D,G and 2D peaks

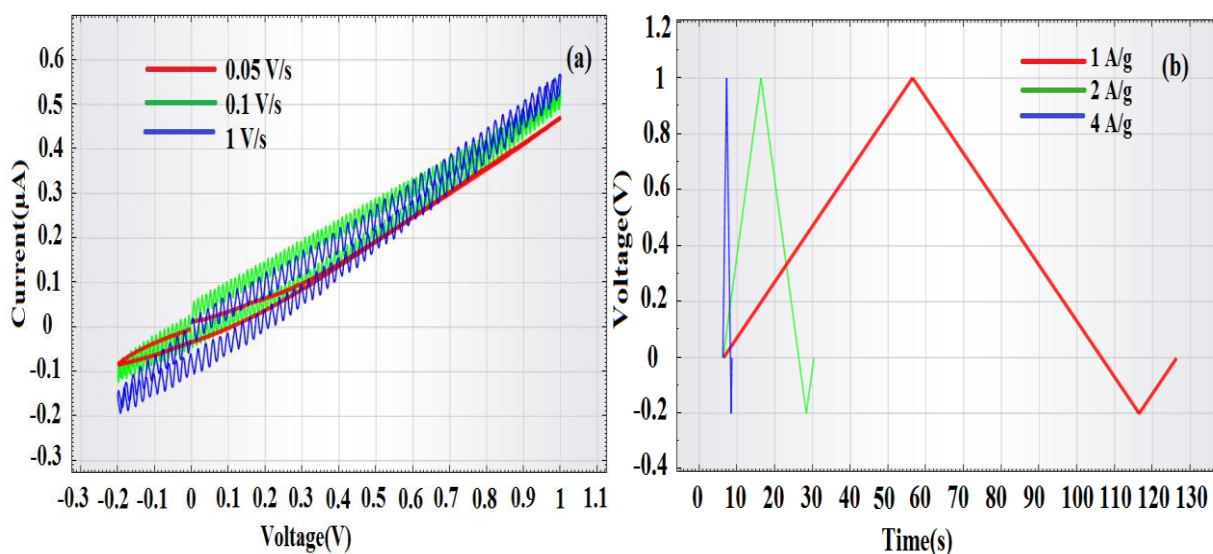
The observed absorbance peak close to the standard value is characteristics of graphene ( Fig.3(a) ) as reported in the literature[13].The highest absorbance value near characteristic peak shows the presence of high concentration of graphene in the liquid sample characterized by UV-vis absorbance spectroscopy.

In order to study the formation of graphene and measure the presence of defects/ impurities in the electrochemical exfoliated graphene, the Raman spectra of the samples prepared were recorded and is shown in Fig.3 (b). Raman spectroscopy is the most suitable method for graphene characterization as it is nondestructive, fast and gives the structural information [14]. The results show the presence of characteristics graphene and defect peaks marked as G, D, and 2D peaks. The  $sp^2$  carbon materials exhibit a very sharp peak around  $2500\text{--}2800\text{ cm}^{-1}$  in the Raman spectra. A sharp 2D peak around  $2690\text{--}2700\text{ cm}^{-1}$  in the Raman spectrum is a signature of graphene and can be used to find the number of layers of graphene. It is because as the number of layers of graphene changes the shape of 2D peak also changes in the raman spectrum. The G-peak ( $1580\text{ cm}^{-1}$ ) arises from the stretching mode of carbon bond in graphitic materials, and is common to all  $sp^2$  carbons [15]. It is highly sensitive to strain effects in  $sp^2$  system; thus, it can be used to probe modification on the surface of graphene. The D-peak represents defects and disorder present in the structure of graphene. The presence of 2D peak in the Raman spectrum confirms the formation of graphene, but due to surface strain of multilayer graphene sheets D peaks has intensity comparable to the G peak. Conducting electrodes for paper supercapacitor were made by brush coating the graphene ink(Fig.4(a)) on A4 size printing paper as shown in Fig.4(b). After each coating the paper was dried for 2 hours at room temperature before the next coating. A total of six layers of coatings were done to form the electrodes. Gel electrolyte was formed by mixing 6 g of PVA (polyvinyl alcohol) with molecular weight of 20000, in 60 ml of water. Then this mixture was stirred for 2 hours until the solution becomes homogeneous with a magnetic stirrer at a temperature of 80 degrees. After 2 hours, 6 g of 1 M  $\text{H}_2\text{SO}_4$ , was added in it while stirring.



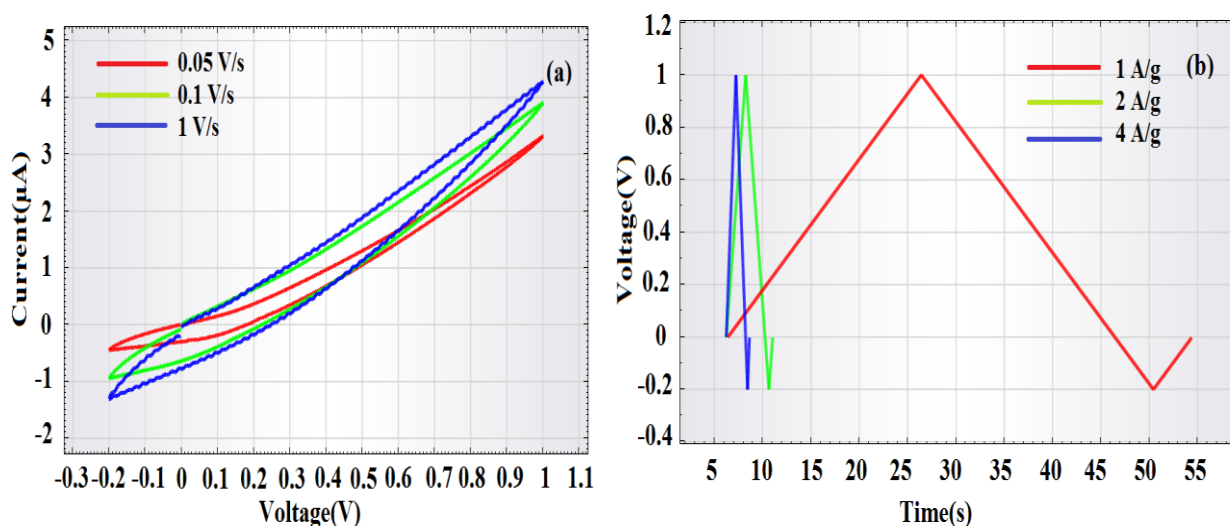


**Figure 4.** (a) Graphene ink (b) Graphene coated conducting paper electrodes (c) Schematic diagram of paper supercapacitor (d) As prepared graphene based supercapacitor

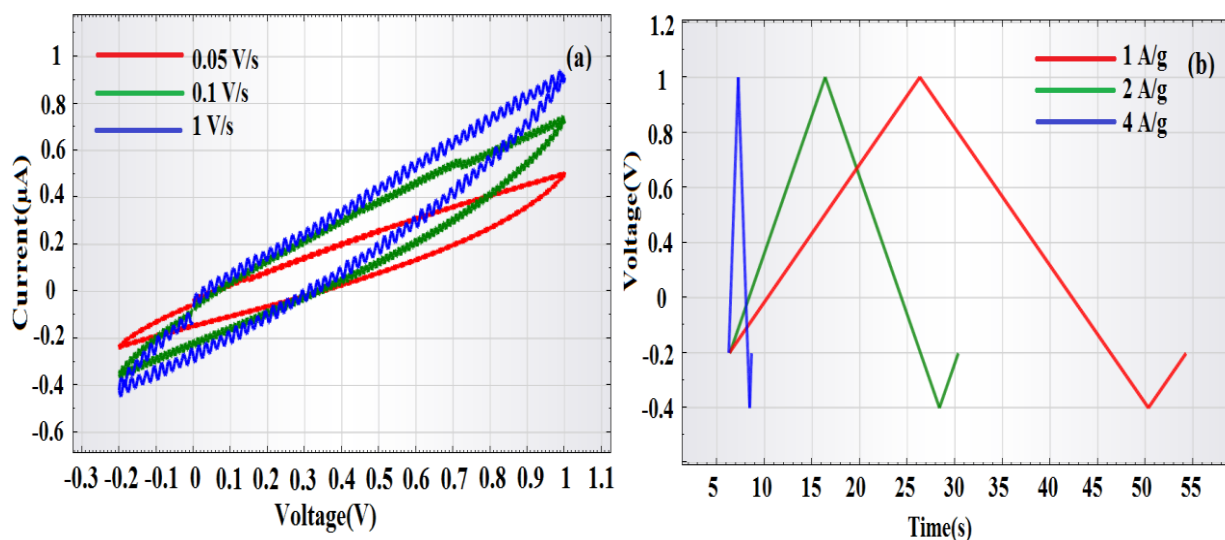


**Figure 5.**(a)Cyclic voltammety (CV) curve (b) Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolyte.

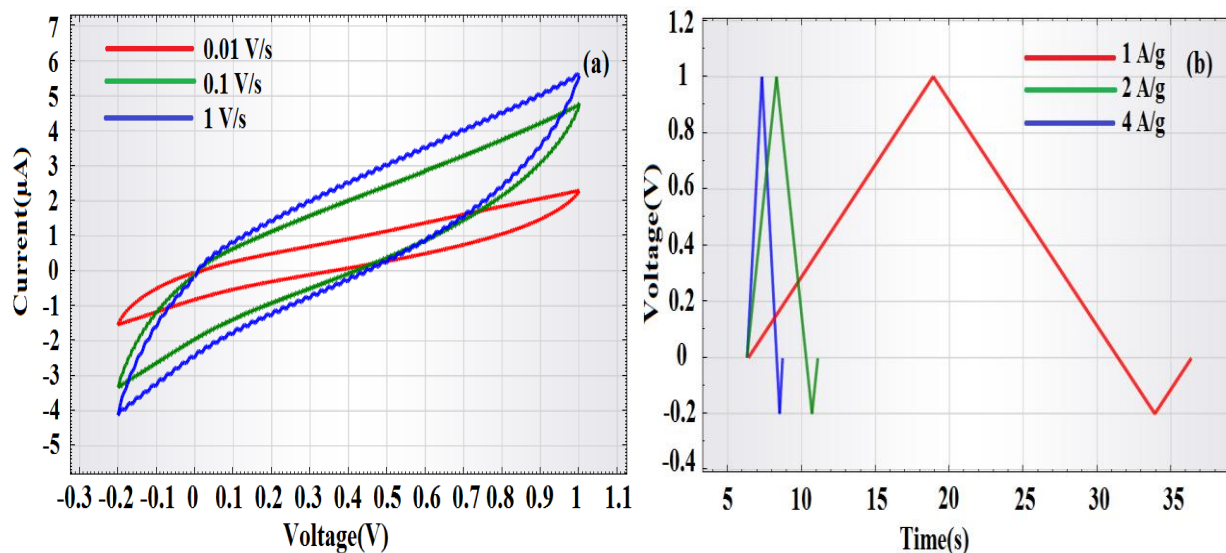
The solution was cooled at room temperature to form the PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolyte. The same procedure is repeated for 1 M each of KOH, KCL, and KNO<sub>3</sub> to form PVA/KOH, PVA/KCL, and PVA/KNO<sub>3</sub> gel electrolytes. Two conducting electrodes of 4 cm<sup>2</sup> area were joined by the gel electrolyte as the separator between them as shown in Fig. 4 (c) and Fig. 4(d). The aluminum foils were used to make contacts electrodes for Cyclic Voltammetry (CV) measurement of the supercapacitor. The area under CV curve is directly proportional to the capacitance of the supercapacitor. The type of the gel electrolyte used effects the specific capacitance of the supercapacitor.



**Figure 6.** (a)Cyclic voltammetry (CV) curve (b) Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KCL gel electrolyte.



**Figure 7.** (a)Cyclic voltammetry (CV) curve (b) Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KNO<sub>3</sub> gel electrolyte.



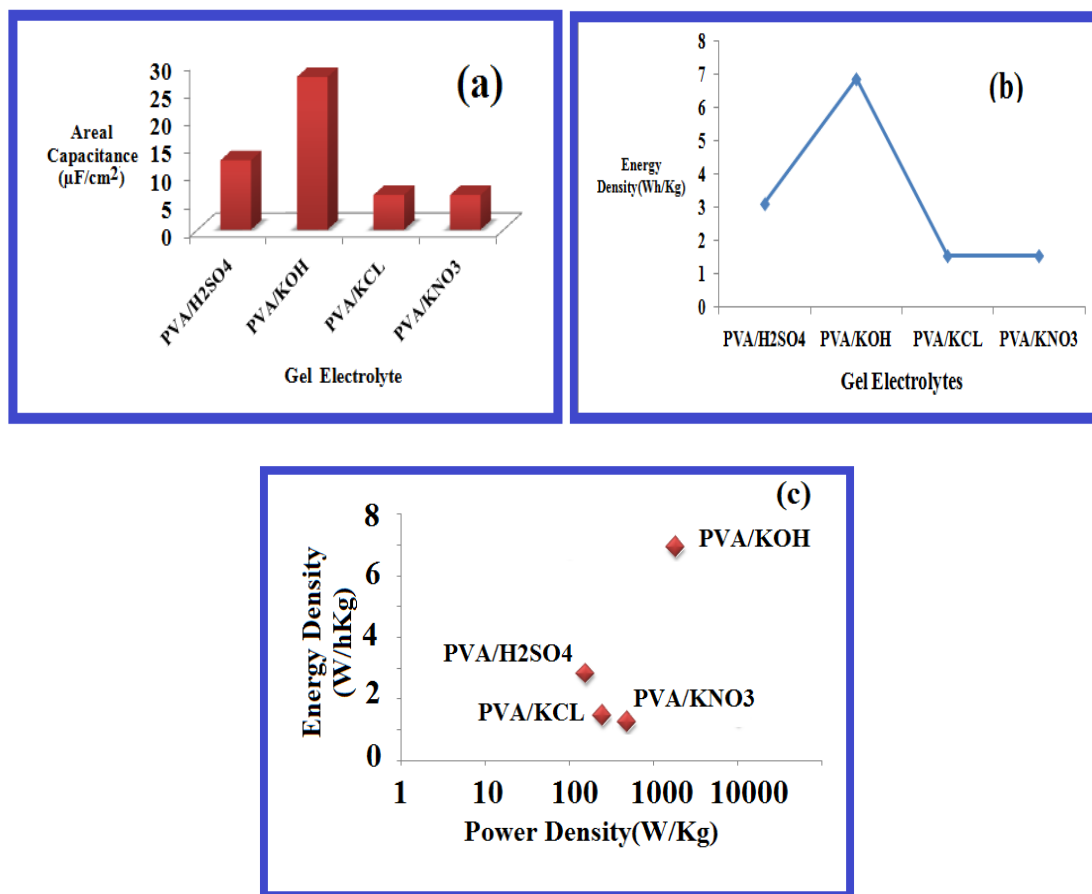
**Figure 8.** (a)Cyclic voltammetry (CV) curve (b) Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KOH gel electrolyte.

#### 4. SUPERCAPACITOR PERFORMANCE EVALUATION

The performance of the flexible supercapacitors was evaluated by cyclic voltammetry (CV) curve and galvanostatic charge discharge (CD) curves. From the galvanostatic charge/discharge curve specific (areal) capacitance, energy density and power density is calculated. Fig.5.(a) shows the Cyclic voltammetry (CV) curve and Fig.5 (b) shows the Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolyte. Fig.6.(a) shows the Cyclic voltammetry (CV) curve and Fig.6 (b) shows the Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KCL gel electrolyte. Fig.7.(a) shows the Cyclic voltammetry (CV) curve and Fig.7.(b) shows the Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KNO<sub>3</sub> gel electrolyte. Fig.8.(a) shows the Cyclic voltammetry (CV) curve and Fig.8.(b) shows the Galvanostatic charge discharge curve of Graphene supercapacitor made by using PVA/KOH gel electrolyte. Areal capacitance was calculated from the charge discharge curve by using the formula  $C = I\Delta t / A\Delta V$ ; where  $I$  is the Current and  $\Delta t$  is the discharging time.  $A$  is the area of active material and  $\Delta V$  is potential Window width from minimum voltage to maximum voltage. Energy density is calculated by  $CV^2/2$ . where  $C$  is the Specific (areal) Capacitance calculated,  $V$  is the width of the potential window. Power density is calculated by  $E/\Delta t$ , where  $E$  is the Energy density and  $\Delta t$  is the discharge time taken by the supercapacitor from maximum voltage to minimum voltage. Specific areal capacitance of the supercapacitor using four gel electrolytes PVA/H<sub>2</sub>SO<sub>4</sub>, PVA/KNO<sub>3</sub>, PVA/KCL, PVA/KOH was calculated and plotted in Fig.9(a). We observe that PVA/KOH gel electrolyte exhibited maximum specific areal capacitance of 30  $\mu\text{F}/\text{cm}^2$  as compared to other gel electrolytes. In this work, it has been observed that areal capacitance obtained by using PVA/KOH gel electrolyte was greater than 2.2  $\mu\text{F}/\text{cm}^2$  as reported earlier by PVA/KOH gel electrolyte[12]. It was also greater than the areal capacitance obtained by PVA/NaOH i.e. 2.4  $\mu\text{F}/\text{cm}^2$  and by using PVA/NaCl gel electrolyte i.e. 0.5



$\mu\text{F}/\text{cm}^2$  as reported earlier[12]. Fig.9 (b) shows the comparison of energy densities obtained by using four different gel electrolytes. Fig.9(c) shows the Ragone plot from the calculated power densities of four gel electrolytes.



**Figure 9.** (a) Comparison of areal capacitances obtained by supercapacitors using different gel electrolytes, (b) Comparison of Energy densities of supercapacitors using four different gel electrolytes,(c) Ragone plot showing the comparison of four gel electrolytes.

The size of the ionic radius of the salt based electrolytes is larger than that of acidic electrolytes which usually results in lower specific capacitance as compared to acidic electrolytes, because larger ionic radii results in lesser penetration of ions in graphene layer. Moreover, the specific capacitance of the supercapacitor becomes large for higher rate of formation of electrical double layer by the cations and anions[16]. The rate of formation of electrical double layer depends upon the charge density of the ions of the electrolytes. Higher the charge density of the ions, faster the formation of electrical double layer which results in higher specific capacitance. The observed value of larger specific capacitance in KOH based electrolyte as compared to H<sub>2</sub>SO<sub>4</sub>, KCL based electrolytes is in accordance with reported work in literature [16]. We believe that the higher charge density of OH<sup>-</sup> (in KOH) as compared to CL<sup>-</sup> (in KCL) and SO<sub>4</sub><sup>2-</sup> (in H<sub>2</sub>SO<sub>4</sub>) ions may be the reason for the higher value of specific capacitance obtained in PVA/KOH as compared to PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolytes.

## 5. CONCLUSION

Synthesis of single and multilayer Graphene nanosheets via liquid phase exfoliation of graphite in DMF organic solvent has been performed. The absence of harsh chemicals like strong acids, reducing agents etc. make this method much simpler than the Hummer's method. The characterization is done using SEM, TEM, UV-spectroscopy and Raman spectroscopy. The graphene paper electrodes made by brush coating method were used to make supercapacitors with four different gel electrolytes and their performance was analyzed by Cyclic Voltammetry and galvanostatic charge discharge measurement. We found that maximum specific areal capacitance of  $30 \mu\text{F}/\text{cm}^2$  was exhibited by PVA/KOH gel electrolyte. This new gel electrolyte has been found to be more effective in comparison to PVA/H<sub>2</sub>SO<sub>4</sub> electrolyte which is most commonly used for making flexible supercapacitors.

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