Synthesis, Characterization of Polyvinyl Alcohol with Graphene Thin film and Investigation of their Super Capacitance Behaviour

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Abstract

Graphene with PVA thin films was coated on glass substrate at different compositions. FTIR spectra of the thin films was confirmed material at particular stretching vibrations and domains. The spectrum seems to conclude the proper formation of the graphene and PVA nanoparticles composites. Suppressions of bands of PVA particle in thin film confirm the blending and effect of graphene. X-ray diffraction pattern for the graphene / PVA blend thin film is shown X-ray Diffractometer (XRD-6000) was run at 40 kV, 30 mA current with a scan speed of 4.00 deg/min and a step of 0.02° using Cu Kα(1.4506 Å graphene crystal is observed in composite films. The gain of crystallinity due to increase in concentration of graphene. SEM morphology imagesshows that the strength of the films. Topographical study of AFM spectra shows that fault, roughness and more physical power of the film. Cyclic voltammograms were recorded electrochemical capacitance study,polarisation behaviour of graphene - PVA thin films.

Keywords: Graphene, PVA, FTIR, Electrochemical, AFM, SEM

1. Introduction

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Advanced thin film technology has expertise in custom coatings and patterned substrates. Technology supporting customers involved with sensors, flat panel displays, Micro-Electro-Mechanical Systems (MEMS), microcircuits, biomedical devices, optical instruments, microwave communications, integrated circuits and microelectronics in general.

Rapid developments in thin film technologies have been encouraged by the growing importance or microelectronics. The development of semiconductor science and technology has been increasingly in the direction of devices utilizing thin film materials which offer the advantage over bulk crystals in many aspects and in terms of material requirements .Layer-by-layer growth yields atomistically smooth films, oriented growth, where grains develop orientation, generally yields rather rough surfaces. Graphene, as a single layer of carbon atoms in a two-dimensional honeycomb crystal lattice, has been attracting tremendous interest in the fields of electronics and composite

materials because of its fascinating properties [1]. There is intense interest in graphene in fields such as physics, chemistry, and materials science, among others. Interest in graphene's exceptional physical properties, chemical tunability, and potential for applications has generated thousands of publications and an accelerating pace of research, making review of such research timely. Here is an overview of the synthesis, properties, and applications of graphene and related materials (primarily, graphite oxide and its colloidal suspensions and materials made from them), from a materials science perspective CNTs [2-7].PVA matrix was prepared in thin film form on chemically cleaned glass substrates by dip coating technique.

Electrochemistry as known to most chemists deals with numerous rather different subjects ranging from energy storage and conversion over analytical methods, synthetic procedures, surface treatment, and corrosion up to bio electrochemistry and beyond. Because of the extreme width of subjects and the sometimes rather specialized applications well established in investigations of the structure of electrochemical interfaces, i.e. in the most basic case the phase boundary between e.g. a solid metal and an aqueous electrolyte solution, have been limited for a long time to the application of traditional electrochemical methods wherein voltage/potential, current, charge and some other experimental variables like temperature, concentration or pressure were either measured or varied. Based on the application of numerous spectroscopic and surface science methods details of the interface at the atomic and molecular level could be elucidated

The aim of this work was to develop the graphene– PVAbased blend with best overall performance, using blending technologies [8-9]. Thermosetting plastics of PVA are attractive because of its high abrasion resistance, tensile and tear strength, flexibility and shock absorbing capabilities. However, it has certain advantages like moderate thermal stability and mechanical strength, limitations in chemical resistance and progression ability. The effect of graphene on the dispersibility was studied [10-11].

The synthesized thin film composite or thin film Nano composite were characterized by Fourier Transform IR spectroscopy, Atomic Force Microscopy (AFM), X-RayDiffractirometer(XRD)[12],scanning electron microscopy (SEM) and Electrochemical Workstation. From the SEM micrograph, the thickness of PVA barrier layer was estimated.

2. Materials and Methods
2.1 Chemicals

All reagents $HAuCl_4$ (Merck), 0.1 M H_2SO_4 (pH 1.0), B.R Buffer (pH 4.0), 0.1M KCl (pH 7.0), B.R Buffer (pH9.2) and 0.1 M NaOH (pH 13.0) were of analytical grade, obtained from Merck (India) Ltd. and used as received without further purification. Ultra pure deionized water was used throughout the experiments.

2.2 Preparation of Graphene /PVA Blend Thin Film on Glass Plate

The various concentrations of graphene (5 mg, 10 mg, 15 mg, 20 mg) uniform mixed with 2 ml of deionized water and sonicated to 20 min at the frequency 53 KHz and bath temperature 30° C to get homogeneous dispersion of graphene. Then 5 mg of PVA was added slowly into the same vessel and sonicated to 30 minutes for the formation of colloid blend of graphene polymer mixture. The blended mixture coated on glass plate by using droplet method. Various concentration of polymer blend were prepared for the 1:1 (5 mg of graphene with 5 mg of PVA), 2:1 (10 mg of graphene with 5 mg of PVA), for the 3:1 (15 mg of graphene with 5 mg of PVA) and 4:1 (20 mg of graphene with 5 mg of PVA).

2.3 Characterization Methods

UV-visible spectroscopy analysis was carried out by a UV–visible spectrophotometer Jasco V-530 between 200 and 1100 nm, possessing a scanning speed of 400 nm/min. Cyclic voltammetric studies were done by using computer controlled CH Instruments, model 650C, performed using a single-compartment cell with three electrodes, at room temperature. The surface morphology was studied by computer controlled JEOL JSM-5600 LV. The computer controlled XRD system JEOL IDX 8030 was used to record the X-ray diffraction of samples. The exact Nanometer size of the particle and surface roughness was characterized by computer controlled Nano surf easy scan 2controlle.

3. Results and Discussion
3.1. FTIR Spectroscopy of Graphene - PVA Thin Film

Figure 1 shows the FTIR spectra of graphene particles. The characteristic bands of graphene are observed at 3746, 3647, 1747, 1682, 1568, 1506, 1228, 1035 cm^{-1}. The presence of different type of oxygen functionalities in graphene oxide was confirmed at 3700 cm^{-1} (O-H stretching vibrations), at 1720 cm^{-1} (stretching vibrations from C=O), at 1600 cm^{-1} (skeletal vibrations from unoxidized graphitic domains), at 1220 cm^{-1} (C-OH stretching vibrations), and at 1060 cm^{-1} (C-O stretching vibrations) [13].It is clearly different from graphene oxide. The characteristic bands of PVA are obtained at 3726, 3260, 2906, 1701, 1654, 1560, 1414, 1324, 1141, 1084, 916,627 cm^{-1}. The FTIR

spectra of PVA a broad peak around 3260 cm^{-1} indicating stretching of hydroxyl groups and peaks at 2906 cm^{-1} due to C-H stretching. The spectrum seems to be consistent with that previously reported in literature except the appearance of absorbed (HOH) bending band at 1660 cm^{-1}. Water is probably present since vacuum drying is not used. A relatively broad and intense (OH) absorption stretching band is observed between (3220 – 3448) cm^{-1}, indicating the presence of polymeric association of the free hydroxyl groups and bonded OH stretching vibration. In general the IR absorption bands of PVA are all quite broad and severally overlapped in the 600-1500 cm^{-1} region. There are several reasons for this behaviour, where half of the bulk PVA consists of crystallites embedded in a matrix of glassy material. The difference of symmetry between PVA molecule and in the glass is expected to contribute to two sets of frequencies to the IR spectrum. Slight shift between equivalent frequencies in the two phasesundoubtedly contributes to the overlapping. There must also exist regions of intermediate crystalinity, and the crystalline region themselves have a mixed symmetry due to the random placement of hydroxyl groups along the chain .As well known, the hydroxyl bands are always strongly broadened in hydrogen bonded alcohol, properly as a result of a very pronounced anharmonicity of vibrations .Furthermore O-H-plane bending motion is coupled strongly with other molecular motions that involve frequencies in the range 600-1500 cm^{-1}. The broad O-H absorption stretching vibration is observed a round 3430 cm^{-1} for PVA results from the superposition of multiple polymeric H bonds associated with the crystalline phase and dimeric H bonds associated with the amorphous phase. Nuclear magnetic resonance has shown that PVA possesses an "intermediate" region in addition to the usual crystalline and amorphous phases. Such an intermediate phase has been identified in other polymers, and played a significant role in the hydration of PVA [14]. Figure 1 shows the FTIR spectra of graphene / PVA blend thin film in the ratio 1:1, 2:1, 3:1, and 4:1. As the concentration of graphene increases in the blend the bands for the PVA was reduced. It confirms the blend formation between graphene and PVA.
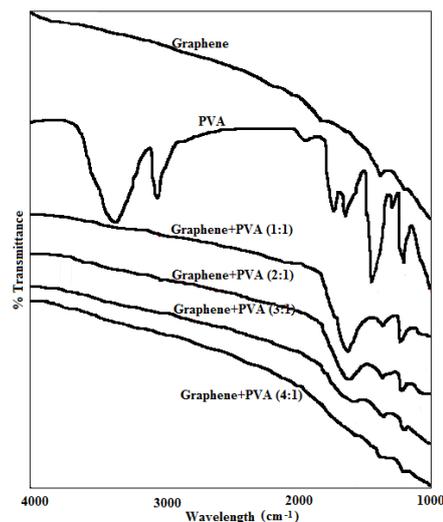

Fig. 1 FTIR spectra of graphene, PVA, graphene+PVA blend in different composition

3.2. X-Ray Diffraction Studies of Graphene - PVA Blend Thin Film

X-ray diffraction pattern for the graphene / PVA blend thin film is shown in Figure 2. X-ray Diffractometer (XRD-6000) was run at 40 kV voltage, 30 mA current with a scan speed of 4.00 deg/min and a step of 0.02° using Cu Kα(1.4506 Å). Graphene / PVA blend thin film shows peak in the following two theta values 26.5445, 54.6671 and 87.0700. The XRD pattern of the graphene / PVA blend thin film revealed a prominent peak of two theta at 26.54 which corresponds to the (002) plane of the graphene crystal is observed. The graphene / PVA blend thin film having an intensity of 8000 for 1:1 ratio and 30000 for 2:1, 3:1, 4:1 ratio. With boost in concentration of graphene thinner, increased and improved intensity in peaks is observed in composite films. The gain of crystallinity due to increase in concentration of graphene. Peaks at 26.5445, 54.6671 and 87.0700 are due to the blend between graphene and PVA.
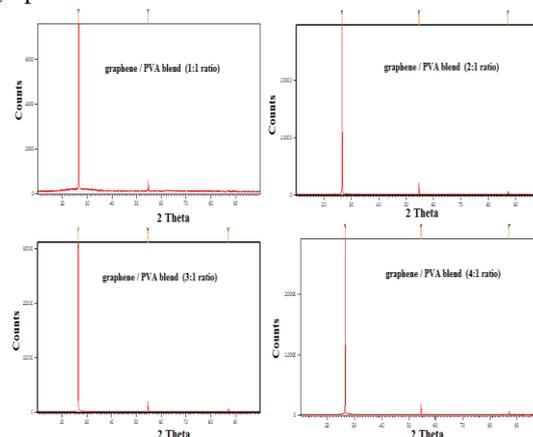

Fig. 2 XRD spectra of graphene+PVA blend in different composition

3.3. SEM Studies of Graphene - PVA Blend Thin Film

SEM images of different concentrations of graphene – PVAcomposite thin films are shown in Fig.3.The observed that in the film with lower concentration of graphene circle shaped particles are seen which are further associated to form clusters of flake on increasing fraction of graphene in the films. On the basis of synthesis process for graphene - PVAcomposite and the SEM photographs, The SEM images suggest that the strength of the films will amplified with rising the concentration of graphene.

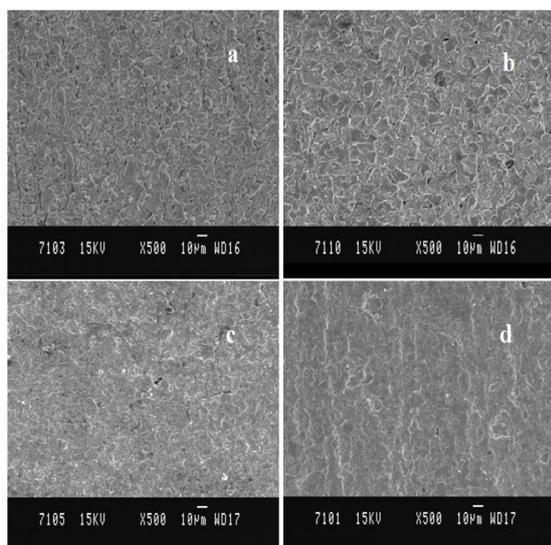Fig.3 SEM image of graphene+PVA blend in different composition a) 1:1, b) 2:1 c) 3:1, d) 4:1

3.4. AFM Spectral Studies of GRAPHENE - PVA Thin Film

AFM spectra were recorded for the graphene - PVA blend thin films on glass substrate. The morphology of the film was studied with AFM under the following conditions: a) scan direction – up b) Time/Line – 206 ms c) Tip voltage - 1V d) Vibration frequency – 169.969 KHz e) Measurement environment – air f) Operating mode – Dynamic force. Figure 4 shows the AFM spectral image of graphene - PVA with different composition (1:1, 2:1, 3:1, 4:1) With 1:1 ratio surface shows small muddle manner and with increase in concentration of graphene it shows the increase in the misdeed, roughness and more physical power of the film. The depth of polymer blends thin film as decreases with increasing the concentration of graphene. These are also proves the incorporation of graphene with PVA and shows more adherent film on glass substrates.
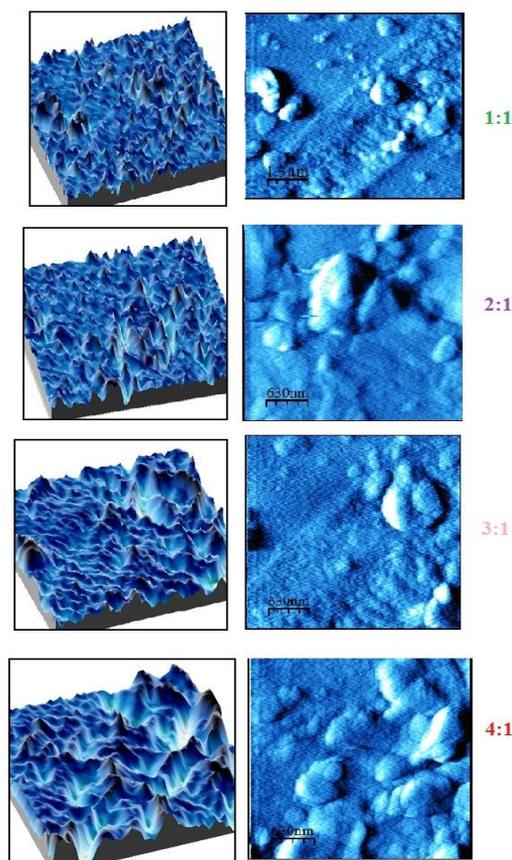

Fig. 4. AFM image of graphene - PVA thin film(1:1 ratio)

3.5. Cyclic Voltammogram Behaviour of Graphene - PVA Blend Thin Film

Cyclic voltammograms were recorded at pH range from 1.0 to 13.0 at a sweep rate 50 mV/s. The coated graphene - PVA blend thin film as working electrode, Ag/AgCl electrode used as reference electrode and platinum electrode is used as counter electrode. Graphene - PVA blend thin film exhibited good responses in all acidic, neutral and basic pH conditions.

3.5.1. Choice of pH

Under identical conditions the cyclic voltammetric results are compared at various pH media. Cyclic voltammetric results of all pH were considered for the correlation. Figure 5 shows the total current vs various pH and the maximum current is observed at pH 7.0. This may be due to faster electron transfer rate at this pH.From this study it is concluded that pH 7.0 is the best pH for the electrochemical capacitance study.
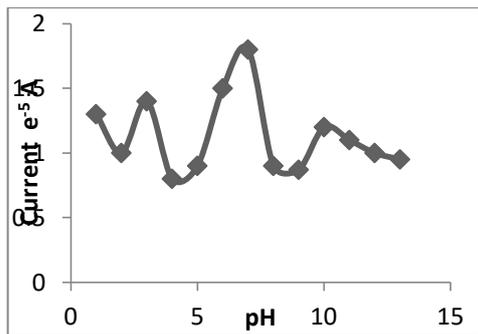
Fig. 5. pH choice of graphene - PVA thin film

3.5.2. Cyclic Voltammetric Behavior of Graphene - PVA blend Thin Film Coated Glass plate at pH 7.0

To study the electrochemical performance of the different concentration of graphene nanostructure materials with PVA as binder, electrochemical measurements were conducted in a three-electrode electrochemical cell with a Pt wire as counter electrode and Ag/AgCl as reference electrode in pH 7.0. In order to illustrate the advantage of the graphene nanostructure materials, Figure 6 the cyclic voltammetry (CV) curves of graphene nanostructure materials at 25 mV s^{-1}. It can be seen that all these curves exhibit nearly rectangular shape, indicating ideal super capacitive behavior. The graphene nanostructure electrode showed a higher integrated area, which reveals the superior electrochemical performance of the graphene electrode. The specific capacitance (C_s) values were calculated from the CV curves using the following equation.

$$C_s = \frac{\int I(u)\mathrm{d}t}{m \times v \times \Delta V}$$

Where I is the oxidation or reduction current, dt is time differential, m indicates the mass of the active electrode material, and ΔV indicates the voltage range of one sweep segment. From equation, the calculated C_s value of the graphene electrode is 182.44 F g^{-1} at a scan rate of 25 mV s^{-1}. The effect of sweep rate was studied at pH 7.0 between 25 and 250 mV/s for graphene - PVA blend thin films (1:1, 2:1, 3:1, 4:1) As the sweep rate increases the background current was also increased, which proves the capacitor behavior of the thin film. Figure 6 shows the cyclic voltammetric behavior of graphene - PVA blend thin film at pH 7.0. At different scan rate studies values are present in (25, 50, 100, 150, 200 and 250 mV/s) table 1. The effect of scan rate on graphene - PVA blend thin films increases (1:1, 2:1, 3:1, 4:1) in pH 7.0 increasing the background current also. The reason may be that insufficient time available for ion diffusion and adsorption inside the smallest pores within a large particle at high scan

rates. It can be seen that the curves were linear and exhibited a typical triangular shape which indicated good electrochemical capacitive characteristics. The enhanced electrochemical performance of the graphene can be attributed to the sandwiched structure. Here, the graphene in the hybrid electrode provides better electronic conductivity and excellent interfacial contact, which results in the fast transportation of electrons throughout the entire electrode matrix.

Additionally, the specific capacitance values decreased with increasing current density. However, the present values are higher than the previously reported even at high current density. The average energy density (E) and power density (P) were derived from the CV curves at different scan rates using the following equations

$$E = \frac{0.5 \times C(\Delta V)^2}{3.6}$$

$$P = \frac{E \times 3,600}{\Delta t}$$

Where E is the average energy density of the electrode (W h kg^{-1}), P is the average power density (W kg^{-1}), C is the specific capacitance of the active material (F g^{-1}), ΔV is the voltage range of one sweep segment, and Δt (s) is the time for a sweep segment. The calculated average energy density and power density of the graphene electrode were approximately 227.68 W h kg^{-1} and 6830.4 W kg^{-1}, respectively, at a scan rate of 25 mV s^{-1}. Similarly other scan rate also calculated and presented in table 2.
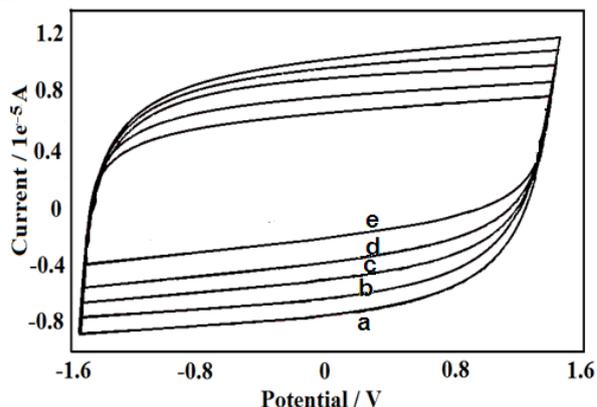

Fig. 6. Cyclic voltammetry (CV) curves of a) graphene and graphene - PVA blend thin film b) 1:1 c) 2:1 d) 3:1e) 4:1

Table 1. Total current for graphene - PVA thin film (**1:1, 2:1, 3:1, 4:1**) at different scan rate in pH 7.0.

Scan rate(mV/s)	current (E^{-5} A)			
	1:1	2:1	3:1	4:1
25	1.423	0.853	1.74	1.527
50	2.369	1.813	2.055	3.075
100	6.845	5.835	6.703	4.894
150	11.765	12.963	10.629	9.286
200	14.682	16.694	15.936	14.967
250	17.572	20.274	19.964	19.738

Table 2. Super capacitor, energy density and power density for graphene - PVA thin film (P1) at different scan rate in pH 7.0.

□(V/s)	Cs (F g^{-1})	E(W h kg^{-1})	P(W kg^{-1})
0.025	182.144	227.68	6830.4
0.050	75.808	94.76	5685.6
0.100	54.760	68.45	8214.0
0.150	41.831	52.29	9412.0
0.200	29.364	36.71	8809.2
0.250	22.416	28.12	8434.6

1.1 3.6. Polarization Behavior of GRAPHENE - PVA Thin Film

These studies carried out by using electrochemical work station (CH650C) from these studies observed that the change in potential with change in concentration of graphene. At different concentration of graphene (1:1, 2:1, 3:1 and 4:1) we observed that the potential also varied from -0.20 to -0.34. The potentials for 1:1 is -0.2143V, for 2:1 is -0.3216V, for3:1 is -0.3426V, for 4:1 is -0.2978V. The change in potential is due to increase in concentration of graphene. Figure 7 shows the tafel plot of various concentration of graphene.
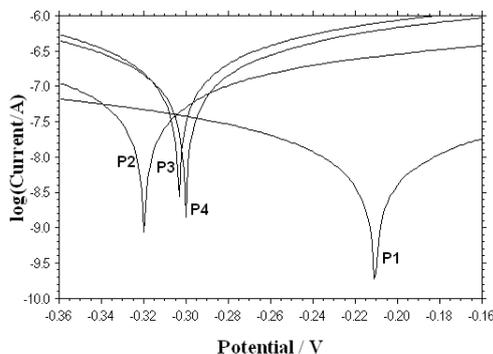

Figure 7 Tafel plot of graphene - PVA thin film (**1:1, 2:1, 3:1, 4:1**)

3.7. Capacitance Behaviour of GRAPHENE - PVA Thin Film

1.2 3.7.1. Capacitance Vs Potential

The capacitances were studied by using electrochemical workstation (CH650C) for various concentrations of graphene with PVA were studied. The applied potential is from -2.0 V to + 2.0 V. For the 1:1 (5 mg of graphene with 5 mg of PVA) and 2:1 (10 mg of graphene with 5 mg of PVA) initially the capacitance value is slowly increasing in the range of 3.8 E^{-11} F, 6.14 E^{-11} F respectively up to -0.20 V, then it is drastically increased with changing potential from -0.2 V to 2.0 V the capacitance value is 4.7 E^{-11} F , 7.8 E^{-11} F respectively and it is in the increasing trend, shown in the Figure 8. For the 3:1 (15 mg of graphene with 5 mg of PVA) and 4:1 (20 mg of graphene with 5 mg of PVA) initially the capacitance value is slowly decreasing in the range of 1.30 E^{-10} F, 1.53 E^{-10} F respectively up to 0.4 V and -0.40 V, then it is drastically increased with changing potential in positive from -0.2 V to 2.0 V the capacitance value is 2.1 E^{-10} F , 1.9 E^{-10} F respectively and it is in the increasing trend, shown in the Figure 8. This increases value of capacitance with change in potential due to increase in concentration of the graphene in blend composition. So from these studies it is observed that the graphene / PVA blend system behaves like good capacitor.
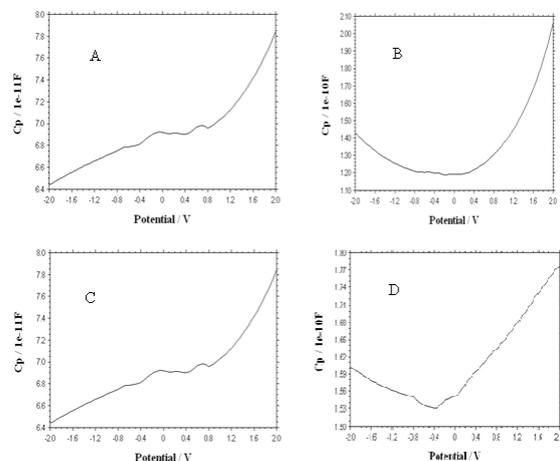

Figure 8 Plot of Capacitance Vs Potential for graphene - PVA thin film(**1:1, 2:1, 3:1, and 4:1**)

3.7.2. Capacitance Vs Time

The capacitance behaviour was studied through electrochemical workstation (CH650C). For various concentrations of graphene with PVA polymer blend thin film were studied. The time is varied from 0 to 10 minutes.

For the 1:1 (5 mg of graphene with 5 mg of PVA) initially the capacitance value is 4.7 E^{-11} F and then it is gradually increased with changing the time up to

10minutes. At 10minutes the capacitance value is 5.0 E^{-11} F it was shown in the Figure 9 (A). For the 2:1 (10 mg of graphene with 5 mg of PVA) initially the capacitance value is 5.7 E^{-11} F and then it is gradually increased with changing the time up to 10minutes and showing 7.7 E^{-11} F steadily after 300 seconds, it shown in Figure 9 (B). 3:1 (15 mg of graphene with 5 mg of PVA) initially shows higher the capacitance value around 1.85 E^{-10} F after 250 seconds it decreased and shows the capacitance value around 1.75 E^{-10} F steadily in Figure 9 (C). 4:1 (20 mg of graphene with 5 mg of PVA) initially shows higher the capacitance value around 2.8 E^{-10} F after 50 seconds it started decreasing and reached the capacitance value around 1.9 E^{-10} F it shown in figure 9 (D). Comparatively the graphene / PVA blend shown good capacitance behaviour for 1:1, 2:1, 3:1Vs time.
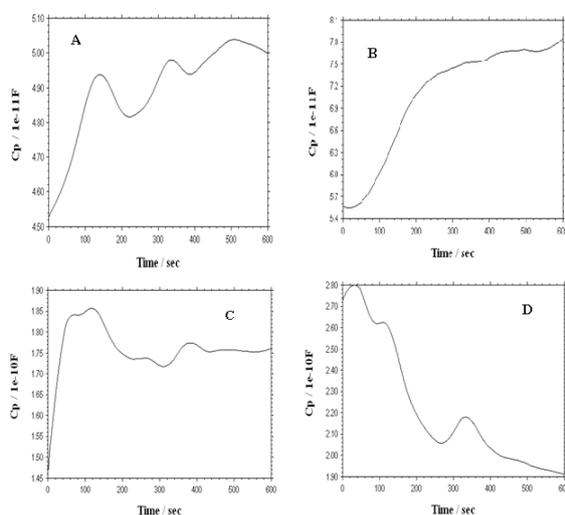

Figure 9. Plot of Capacitance Vs time for graphene - PVA thin film (**1:1, 2:1, 3:1, 4:1**).

Conclusion

Graphene with PVA as binding agent nanostructure material thin films was coated on glass plate at different compositions. FTIR spectra recorded for graphene particles, PVA and graphene /PVA thin films on glass plate to conclude the proper formation on blending between the graphene and PVA particles. Suppressions of bands of PVA particle in thin film confirm the blending and effect of graphene. X-ray diffraction pattern for the graphene / PVA thin film shows the gain of crystallinity of film due to increase in concentration of grapheme SEM images that the strength of the films will amplified with rising the concentration of graphene. AFM spectra of thin films shows that increase in concentration of graphene shows the increase in the misdeed, roughness and more physical power of the film. Cyclic voltammograms were recorded in the pH range from 1.0 to 13.0 and from this study it is

concluded that pH 7.0 is the best pH for the electrochemical capacitance study.The effect of sweep rate was studied between 25 and 250 mV/s thin films at pH 7.0 was shows good agreement of capacitor behavior. Polarisation behaviour of graphene - PVA thin films were studied and the potential also varied from -0.20V to -0.34V. Capacitance behaviour of thin films were studied Vs potential and time, it behaves like good capacitor.The average energy density of the electrode, the average power density and specific capacitance of the active material is good.We suggest that the graphene – PVA blend can be used for super capacitor applications.

Acknowledgement

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