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## ORIGINAL ARTICLE

# Facile electrochemical synthesis of few layered graphene from discharged battery electrode and its application for energy storage

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Received 30 May 2015; accepted 14 August 2015

## KEYWORDS

Few layered graphene;  
Zinc carbon battery;  
Electrochemical expansion;  
Sodium dodecyl benzene sulfonate;  
Supercapacitors

**Abstract** A cost-effective, simple and non-hazardous route for synthesis of few-layered graphene from waste zinc carbon battery (ZCB) electrodes via electrochemical expansion (ECE) has been reported. In this synthesis, we have electrochemically exfoliated the graphene layers, by intercalating sodium dodecyl benzenesulfonate (SDBS) surfactant into graphitic layers at different D.C. voltages with a constant SDBS concentration. The graphene sheets were isolated, purified and characterized by Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), Raman spectrometry, Ultraviolet absorption (UV), Selected area electron diffraction (SAED) and Cyclic voltammetry. Best result was obtained at 4.5 V of D.C. A possible mechanism for the intercalation process has been proposed. A promising application of the produced material for supercapacitor application has also been explored in combination with polyaniline.

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## 1. Introduction

Magical, mother of all graphitic carbon, one atom thick, two-dimensional carbon material graphene has emerged as a new hope for the entire scientific community (Novoselov et al., 2005; Rao et al., 2009) owing to its unique properties including ultrahigh carrier mobility, large surface area, excellent thermal stability, mechanical properties etc. (Nair et al., 2008; Xu et al., 2013; Ohta et al., 2006). Nowadays graphene is treated as a rising star in the field of technological applications, particularly in the fields of high efficiency sensors (Kim et al., 2009), fuel

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Peer review under responsibility of King Saud University.



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<http://dx.doi.org/10.1016/j.arabjc.2015.08.016>

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Please cite this article in press as: Tiwari, S.K. et al., Facile electrochemical synthesis of few layered graphene from discharged battery electrode and its application for energy storage. Arabian Journal of Chemistry (2015), <http://dx.doi.org/10.1016/j.arabjc.2015.08.016>

cells (Qu et al., 2010; Rao et al., 2009), renewable energy sources (Sun et al., 2011; Choi et al., 2010), electrochemical-capacitors (Sun et al., 2011;), transparent electrodes (Stankovich et al., 2006), and nanocomposite materials (Zhang and Liu, 2012; Mukhopadhyay and Gupta, 2011). However, scalable synthesis of bulk pure graphene is still a bottleneck in the path of its fascinating technological applications (Krauss et al., 2009; Mukhopadhyay and Gupta, 2011; Wang et al., 2010). Several routes have been developed for graphene synthesis, each having their own advantages and disadvantages (Mukhopadhyay and Gupta, 2011). Among the various methods viz chemical exfoliation (Marco et al., 2010), chemical vapor deposition (CVD) (Xu et al., 2013), ECE etc. (Hernandez et al., 2008; Wang et al., 2011), ECE of graphite sheet is cheaper, easy and adorably accepted by material scientists. However, most of the reported ECE techniques for graphene synthesis, from graphite, used various hazardous chemicals such as  $H_2SO_4$  and KOH. as electrochemical expansion medium (Tripathi et al., 2013). From the waste management point of view and considering environmental issues (Sun et al., 2011), in this work we have synthesized few layered graphene from graphite electrode extracted from discharged zinc-carbon batteries (ZCBs) using a very low concentration of aqueous sodium dodecyl benzene sulfonate (SDBS). A possible mechanism of electrochemical expansion has been put forward on the basis of fundamental electrochemistry. This simple and one step synthesis process for the production of few layered graphene will be very useful for its application in the field of polymer nanocomposite and new generation ultracapacitors.

## 2. Materials and methods

### 2.1. Materials

Multipurpose ZCBs were obtained from discharged batteries of Eveready Industries India Ltd. Hydrochloric acid (37%) was obtained from Merck specialist private limited, Mumbai. SDBS was obtained from Loba Chemie Pvt. Ltd., Mumbai. Aniline and ammonium persulphate (APS) were obtained from SRL Pvt. Ltd. and CDH private limited New Delhi (India), respectively.

### 2.2. Separation of electrode from used ZCB and treatment

The carbon electrode rod was taken out from discharged battery and was washed with very dil. HCl (20%). The electrode was then boiled in millipore water for about 5 min to remove any remaining impurities. The graphite electrode so obtained was then subjected to electrochemical exfoliation.

### 2.3. Electrochemical exfoliation of ZCB graphite electrodes

The whole electrochemical exfoliation experiments were performed at room temperature. A solution of 0.01(M) SDBS was prepared in distilled water and kept for 15–20 min under constant stirring until it gets completely dissolved. Two waste ZCB graphite electrodes were employed as electrode material and as a source for graphene. For electrochemical expansion one electrode acts as cathode and other as the anode. Both

electrodes were separated by a rubber sheet. The electrolysis was carried out with the help of AC source with DC output current of 500 mA and the overall electrochemical process was carried out for five hours. After completion of ECE, larger graphite particles are collected by centrifugation at 2000 rpm. Then the suspension was filtered by a PTFE membrane and the filtrate was centrifuged again at 10,000 rpm for 10 min to obtain fine graphene and the supernatant was decanted away. The remaining solid material was purified by successively washing with 50 mL of water, 50 mL of 30% HCl, and 50 mL of ethanol. The solid obtained was vacuum-dried overnight at room temperature and weighed. Approximate yield of the product was found to be 0.005, 0.020 and 0.025 grams per hour for 3 V, 4.5 V and 6 V, respectively. Very small amount of sample was collected for 7.5 and 9 V exfoliation voltage due to very fast exfoliation during which bigger particles were separated and removed during first centrifugation step. The particles so obtained were subjected for further characterizations. A schematic diagram of the whole process is presented in Fig. 1.

### 2.4. Preparation of nanocomposites with aniline

Three binary nanocomposites were prepared using synthesized graphene via 3 V, 4.5 V and 6 V ECE. In a typical synthesis, 0.05 g of produced graphene was taken and well sonicated in distilled water till a homogeneous dispersion was obtained. To this, 1 ml aniline was added slowly under constant stirring followed by dropwise addition of APS solution (2.5 g in 50 ml water) and then sonicated. The solution was then refrigerated overnight, filtered, washed and dried to obtain the nanocomposites.

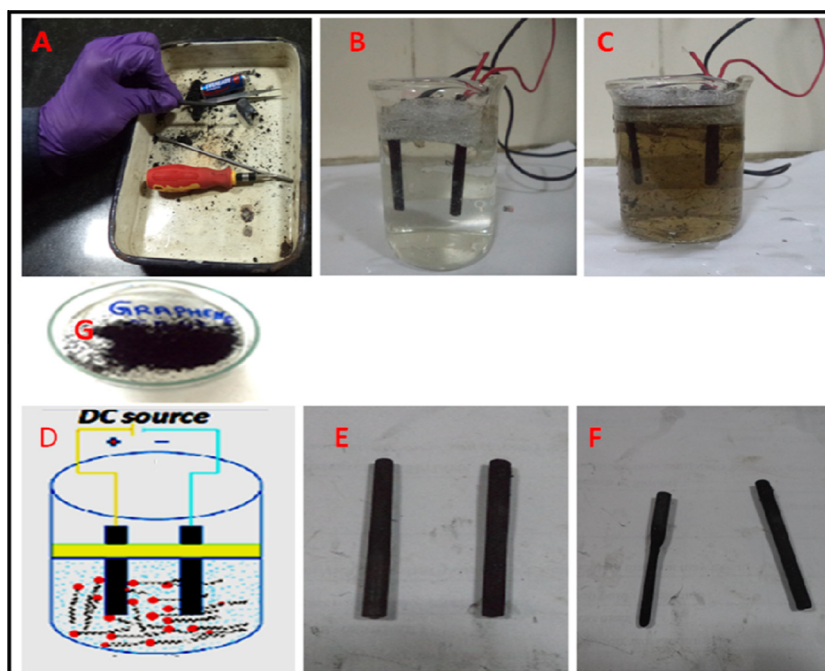
### 2.5. Characterization of prepared few layered graphene and composites

The samples were analyzed using SEM (Hitachi 3400-N), FESEM (supra 55 Carl Zeiss, Germany), TEM (HR-TEM, JEOL 2100), FTIR (Perkin Elmer spectrum RXI), Raman spectroscopy (Horiba JobinYuon, Raman spectrometer model No. H 4551) and XRD (Bruker DS Focus). Cyclic voltammetry study was carried out in CHI760D model in the potential range of 0–0.8 V with various scan rates of 10, 20, 50, 100 and 200 mV/s. Galvanostatic charging/discharging study was also carried out within the same potential window of 0–0.8 V. The working electrode was prepared by dispersing required amount of sample in 5 ml ethanol and one drop nafion as a binder. From this well sonicated mixture uniformly dispersed sample was pipetted out and drop casted over the tip of glassy electrode and dried before electrochemical analysis.

## 3. Results and discussion

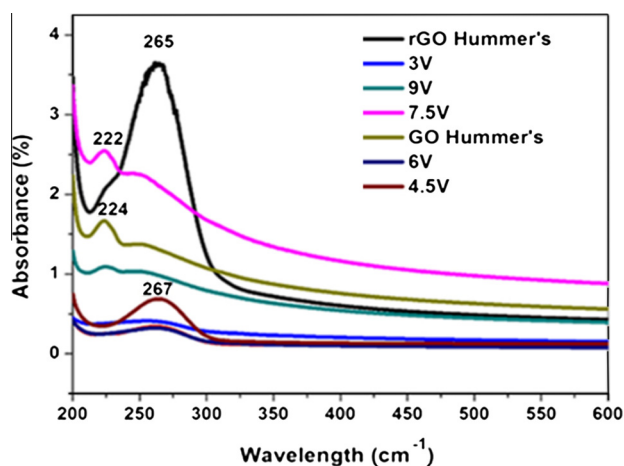
### 3.1. Spectroscopic and microscopic characterization of prepared materials

UV–visible spectra analysis can give insight into the quality and nature of graphene. It has been reported that single-layered, bi-layered and few-layered graphene produces UV–vis absorption around 265 nm due to the  $\pi-\pi^*$  transitions of



**Figure 1** (A) Separation of graphite rod from battery, (B) and (C) Color of solution before and after ECE, (D) ECE process, (E) and (F) Morphology of electrode surface before and after the ECE and (G) Graphene sample prepared by ECE at voltage 4.5 V.

aromatic C—C bonds (Li et al., 2008). Fig. 2 shows a collection of UV spectra of all synthesized samples. We have also prepared graphene by chemical oxidation–reduction method (improved Hummers method and hydrazine reduction) and incorporated its UV spectrum in Fig. 2 for comparison. As shown in Fig. 2, an absorption peak at 267 nm was observed for sample obtained with 4.5 V DC which can be attributed to the  $\pi$ – $\pi^*$  transitions in graphene (Li et al., 2008; Marcano et al., 2010). This peak also matches with the graphene peak obtained by chemical oxidation/reduction method. However, as the potential increased above 6 V i.e. for 7.5 V and 9 V DC, the 265–267 nm absorption peaks disappeared and a

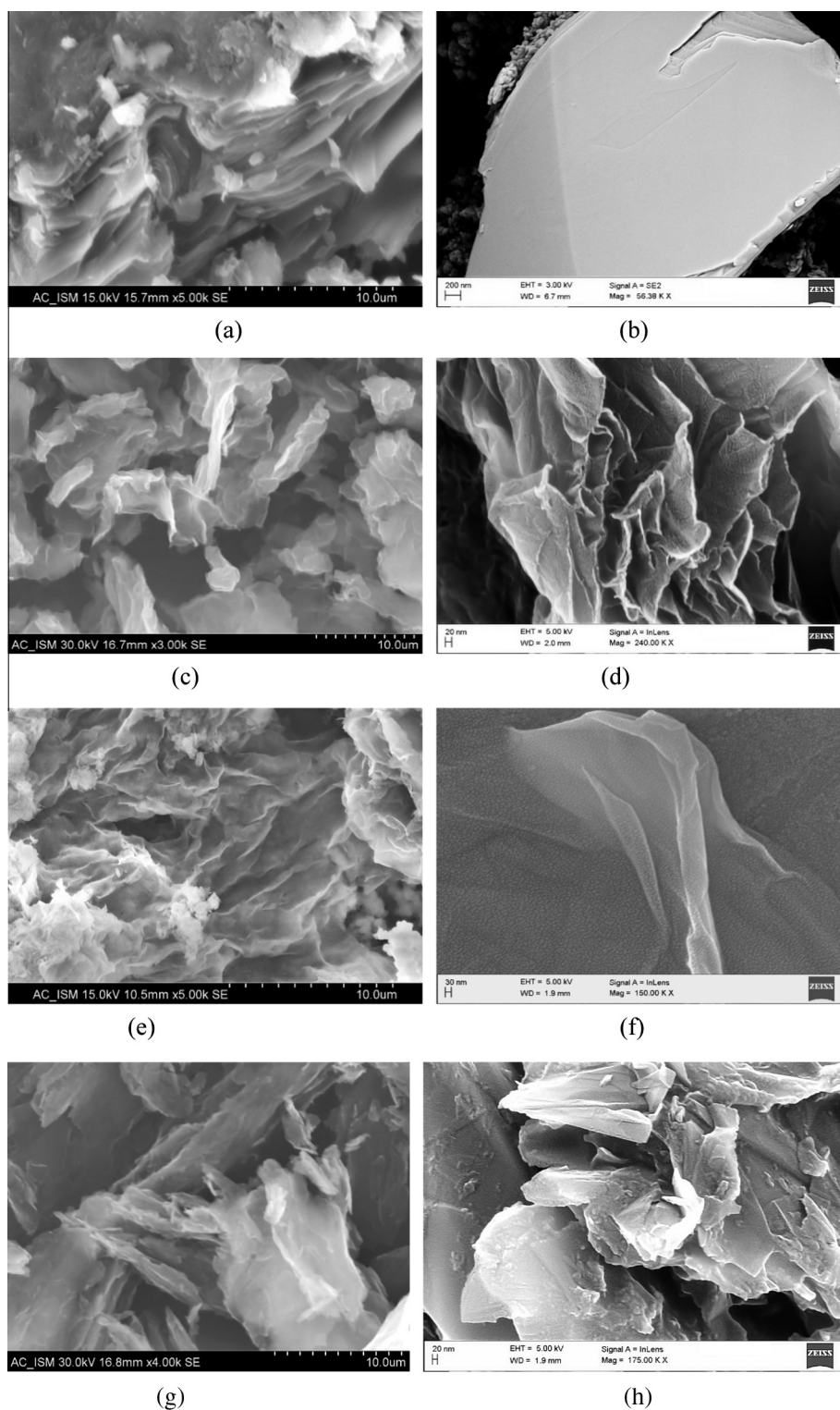


**Figure 2** UV spectra of samples obtained at different ECE voltages.

new peak at 224 nm appeared. This peak around 224 nm can be attributed to graphene oxide (Li et al., 2008; Marcano et al., 2010). So, it seems that once the potential increased above 6 V, the graphite sheets were getting oxidized. The mechanism of this oxidation is not known and further investigations are required for establishing the reaction mechanism. Since we have focused on few layered graphene synthesis, not graphene oxide, we further characterize only the samples obtained at 3, 4.5 and 6 V.

The samples obtained with 3, 4.5 and 6 V were analyzed with SEM and FESEM and are shown in Fig. 3. For comparison, small amount of sample was scratched from the graphite electrode (coded as graphite powder) and also analyzed with SEM and FESEM. Both SEM and FESEM images of graphite powder (Fig. 3(a and b)) show compact rigidly bound graphitic sheets. In contrast to graphite powder, SEM image of samples obtained at 3 V, 4.5 V and 6 V showed exfoliated few layered graphene sheets. FESEM images of 3 V sample depicted that interlayer spacing between graphene sheets increased as compared to graphite powder but 6 V sample showed both exfoliated and ordered multilayered graphene sheets. However, 4.5 V sample showed a well separated graphene sheet which suggested that quality of graphene obtained at 4.5 V is better than other products.

To further analyze the quality of graphene, all three samples were analyzed with AFM and are presented in Fig. 4(a–c) with their respective height profile. It was found that samples obtained at 3 V (Fig. 4(a)), 4.5 V (Fig. 4(b)) and 6 V (Fig. 4(c)) have sheet thickness around 5 nm, 2.5 nm and 6 nm, respectively, which corresponds to few layered graphene. The sample obtained at 4.5 V was analyzed with TEM and SAED and images are presented in Fig. 4d and e. TEM image Fig. 4d clearly demonstrates the transparent and aggregated

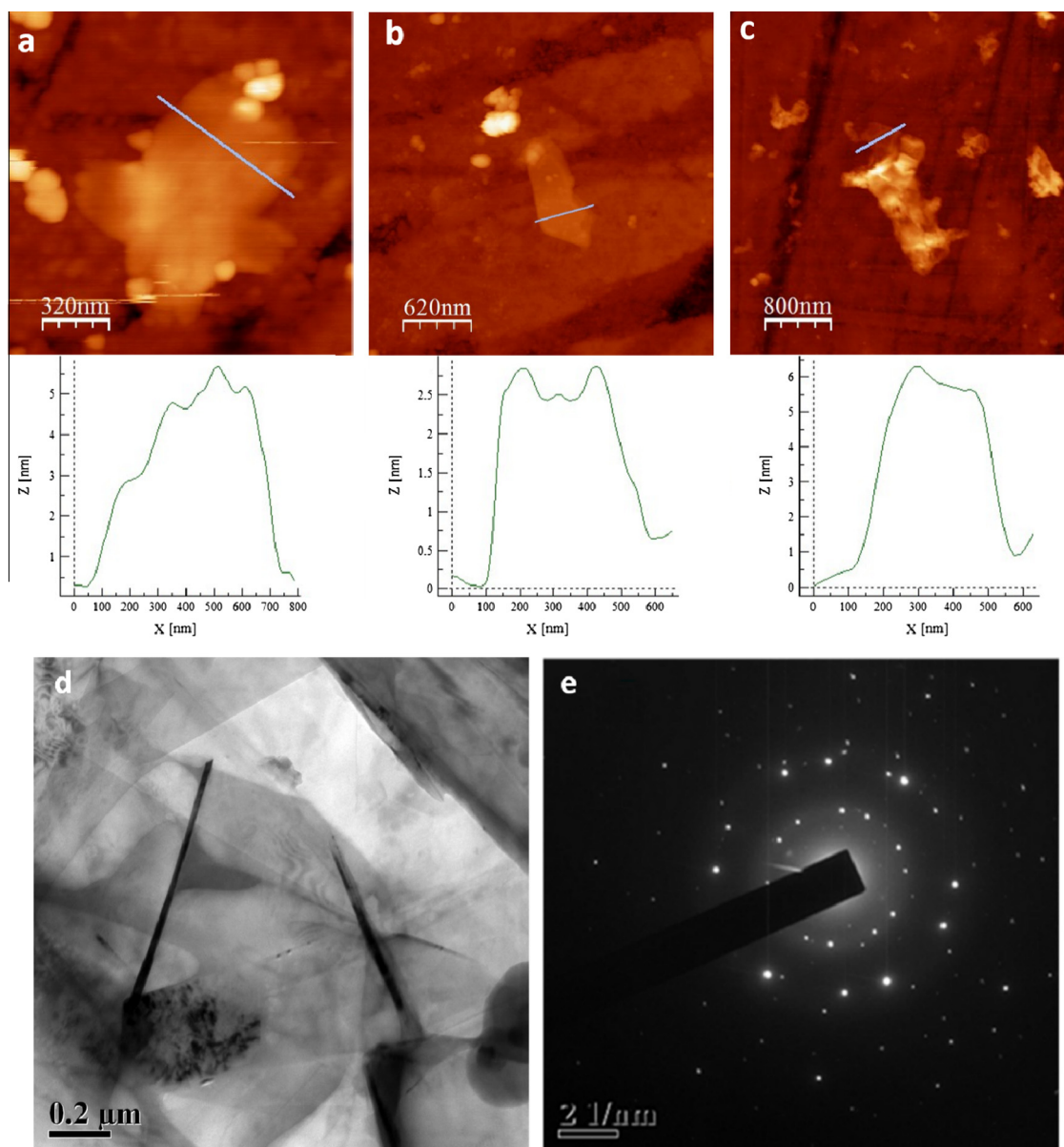


**Figure 3** SEM and FESEM images of (a, b) Graphite powder, (c, d) product obtained at 3 V, (e, f) product obtained at 4.5 V and (g, h) product obtained at 6 V.

few layered graphene. The absence of diffuse diffraction ring pattern and presence of spot pattern in SAED image (Fig. 4e) confirmed the crystalline graphitic layer (Malard et al., 2009). The mechanism and efficiency of exfoliation can be explained on the basis of surfactant molecule intercalation

and exfoliation of graphene sheets during ECE, which has been explained in the mechanism for exfoliation section.

FTIR analysis was employed to investigate the bonding interactions in the prepared graphene samples which are presented in Fig. 5. Two peaks at  $2916$  and  $2850\text{ cm}^{-1}$  are

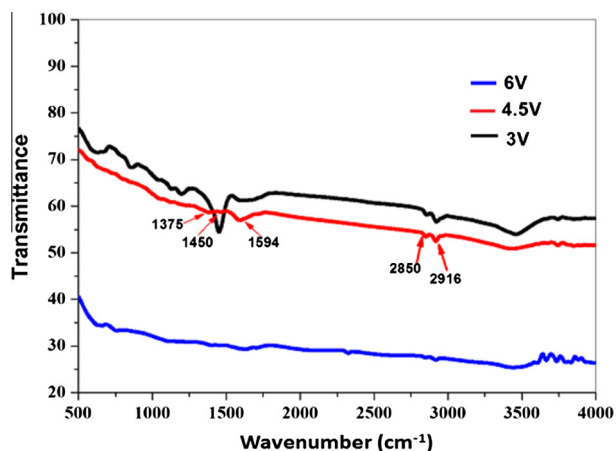


**Figure 4** AFM and corresponding height profiles of samples obtained at (a) 3 V, (b) 4.5 V and (c) 6 V, (d) TEM and (e) SAED images of sample obtained at 4.5 V of ECE voltage.

observed for all the samples which can be attributed to the C–H stretching vibrations of the methylene group and the peak at  $1594\text{ cm}^{-1}$  can be attributed to the aromatic C=C stretching (Tripathi et al., 2013). Absence of any peak around  $1715\text{ cm}^{-1}$  confirmed that the sheets are separated without any oxidation. This further supports the UV analysis where the peak for graphene oxide was missing in the spectra (Tripathi et al., 2013; Marcano et al., 2010).

The samples were further characterized by XRD and plot is presented in Fig. 6. Pure graphite electrode shows up a peak at around  $26.6^\circ$  (inset Fig. 6) corresponding to the (002) plane which indicates an interlayer spacing of 0.34 nm. After electrochemical exfoliation at 3 V DC, the peak at around  $26.8^\circ$  becomes broader and the broadness increases with increase in exfoliation voltage from 3 V to 4.5 V. The disappearance of the sharp peak can be attributed to the exfoliation of lay-

ered structures of graphite. The broad peak may stem from the partial restacking of exfoliated graphene layers (Hulicova et al., 2005; Marcano et al., 2010). In addition, this result shows no characteristic peak of graphene derivatives, indicating that this approach is free of oxidation reactions. Absence of any peak at low  $2\theta$  value indicates that during the course of the electrochemical exfoliation the sheets are completely separated from each other in the form of few-layered graphene (Hulicova et al., 2006; Ohta et al., 2006). As the voltage increased from 4.5 V to 6 V, the characteristic peak of graphite at  $26^\circ$  becomes more prominent. This can be due to the fast electrochemical exfoliation of graphitic layers at higher potential which diminished the time for intercalation of surfactant molecule inside the intergallery and hence multiple stacked graphitic layers broke down from the electrode during the exfoliation process. This analysis evidently shows that



**Figure 5** FTIR spectra of products obtained at 3 V, 4.5 V and 6 V of ECE voltages.

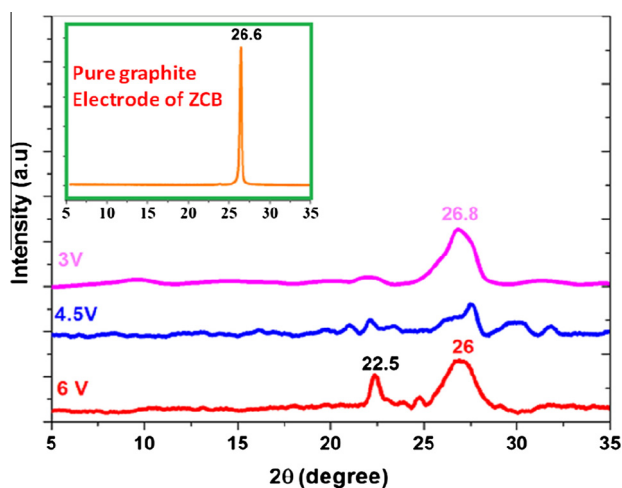
electrochemical process must be optimized to obtain good quality graphene. If the exfoliation potential is too small then the separation of sheet will not occur and if it is too high multiple stacked multilayered sheets will be separated from the electrode.

Raman spectroscopy is the most appealing technique to characterize carbon compounds because of its nondestructive, fast and high resolution analysis, and gives the structural and electronic information (Malard et al., 2009; Vlasiouk et al., 2011). All the  $sp^2$  carbon materials exhibit a very sharp peak around  $2500\text{--}2800\text{ cm}^{-1}$  in the Raman spectra (Malard et al., 2009). A sharp 2D band around  $2690\text{--}2700\text{ cm}^{-1}$  in the Raman spectrum is a signature of  $sp^2$  graphitic system (Malard et al., 2009). The 2D-band is a second-order two-phonon process and frequency dependent on energy of excitation laser. So, it can be used to quantify the number of layers in graphene, because in multi-layer graphene, the shape and nature of 2D band is pretty much different from that in the single-layered and few-layered graphene (Malard et al., 2009). The G-band ( $1580\text{ cm}^{-1}$ ) is due to  $E_{2g}$  mode at the  $\Gamma$ -point and it arises from the stretching mode of C–C bond in graphitic materials, and is common to all  $sp^2$  carbons (Malard et al.,

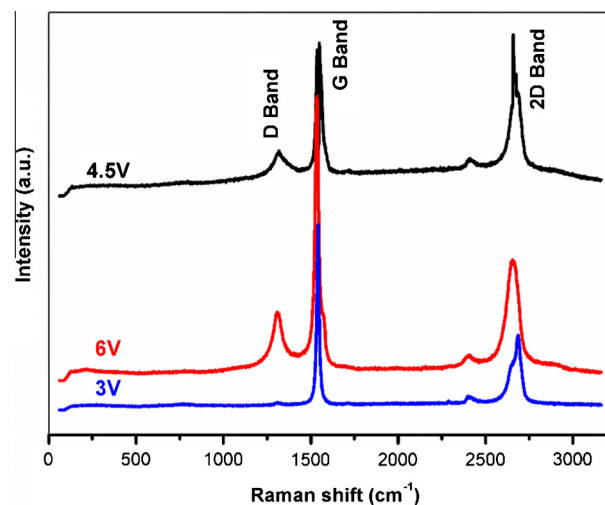
2009; Vlasiouk et al., 2011). It is highly sensitive to strain effects in  $sp^2$  system; thus, it can be used to probe modification on the surface of graphene (Gupta et al., 2006). The D-band represents disordered structure of graphene (mainly  $sp^3$  hybridized carbon atoms) which makes Raman spectroscopy one of the most sensitive techniques to characterize graphene and its derivatives (Malard et al., 2009). Fig. 7 shows the Raman spectra acquired from the graphene samples collected at different ECE voltages. The typical feature of graphene i.e. G-band at  $\sim 1580\text{ cm}^{-1}$  and 2D band at  $\sim 2710\text{ cm}^{-1}$  appears for all the three samples. Apart from these peaks, 4.5 V and 6 V sample shows prominent D-band peak at  $\sim 1350\text{ cm}^{-1}$ . Other defective bands such as D' band ( $1620\text{ cm}^{-1}$ ) and D + G band ( $2947\text{ cm}^{-1}$ ) are absent in all three samples (Malard et al., 2009). In the case of 4.5 voltage, D band is very weak and broad with  $I_G/I_D$  intensity ratio around 4.98 indicating majority of  $sp^2$  hybridized carbon atom throughout the graphene sheet (Vlasiouk et al., 2011). In addition the product obtained at 4.5 voltage also possesses  $I_{2D}/I_G$  ratio equal to one which is a fingerprint of few layered graphene (2–5 layers). However, in the case of sample obtained at 3 V, Raman spectrum is similar to the expanded graphite while for 6 voltage D peak becomes prominent along with decrease in intensity of 2D which is an indication of slight oxidation on graphitic layers (Marcano et al., 2010). Thus, from the experimental observation it seems that both low and high voltages are not suitable for ECE of graphite and it must be optimized to get good quality few layered graphene.

### 3.2. Probable path of graphene formation via ECE

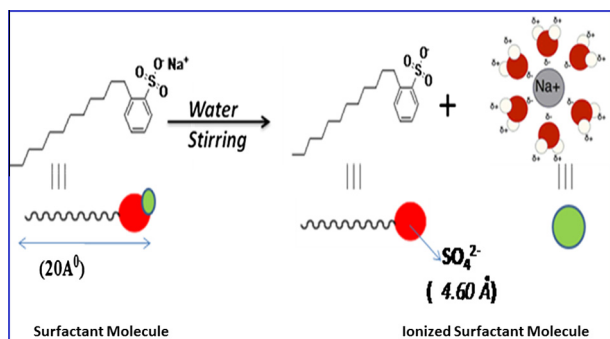
Most of the previously reported ECE, for graphene synthesis, employed  $\text{H}_2\text{SO}_4$  or analogous chemical as electrolyte (Tripathi et al., 2013; Su et al., 2011). In the solution, it generates  $\text{SO}_4^{2-}$  and heavily hydrated  $\text{H}^+$  ions which, because of its very small size, do not play a significant role in the ECE of graphite. On the other hand, the hydration of  $\text{SO}_4^{2-}$  ion in the solution is very low because of its larger size and in the solution it has size of  $\sim 4.60\text{ \AA}$  (House, 2008), which is about  $\sim 1.37$  times larger than the interlayer distance between the graphitic layers ( $3.35\text{ \AA}$ ) (House, 2008; Tripathi et al., 2013;



**Figure 6** XRD pattern of products obtained at 3, 4.5, and 6 V.

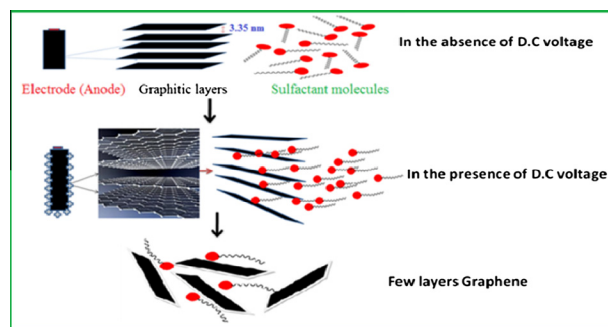


**Figure 7** Raman spectra of products obtained at 3, 4.5 and 6 V.



**Figure 8** Dissociation of SDBS molecules in water and hydration of sodium ion.

Su et al., 2011). Thus, under applied voltage the  $\text{SO}_4^{2-}$  ions intercalate between graphitic layers and being bigger ( $\sim 4.60 \text{ \AA}$ ) and can easily push the graphitic layers farther apart making the spacing greater than  $3.35 \text{ \AA}$ , thereby weakening Van der Waals forces and leading to the formation of graphene. On the basis of similar mechanisms, we employed SDBS surfactant as electrolyte which possesses  $\text{SO}_4^{2-}$  moiety in the solution and functions as an expansion initiator under applied voltage. The added advantage of using SDBS is the size of SDBS which is much larger ( $20 \text{ \AA}$ ) (Palazzesi et al., 2011) than naked  $\text{SO}_4^{2-}$  and it contains a benzene ring which enables  $\pi$ - $\pi$  interaction with graphitic layers yielding greater feasibility of ECE. In addition to this, SDBS is less toxic compared to  $\text{H}_2\text{SO}_4$  and other acidic solutions, and it does not initiate any oxidative reaction during ECE. Dissociation of SDBS

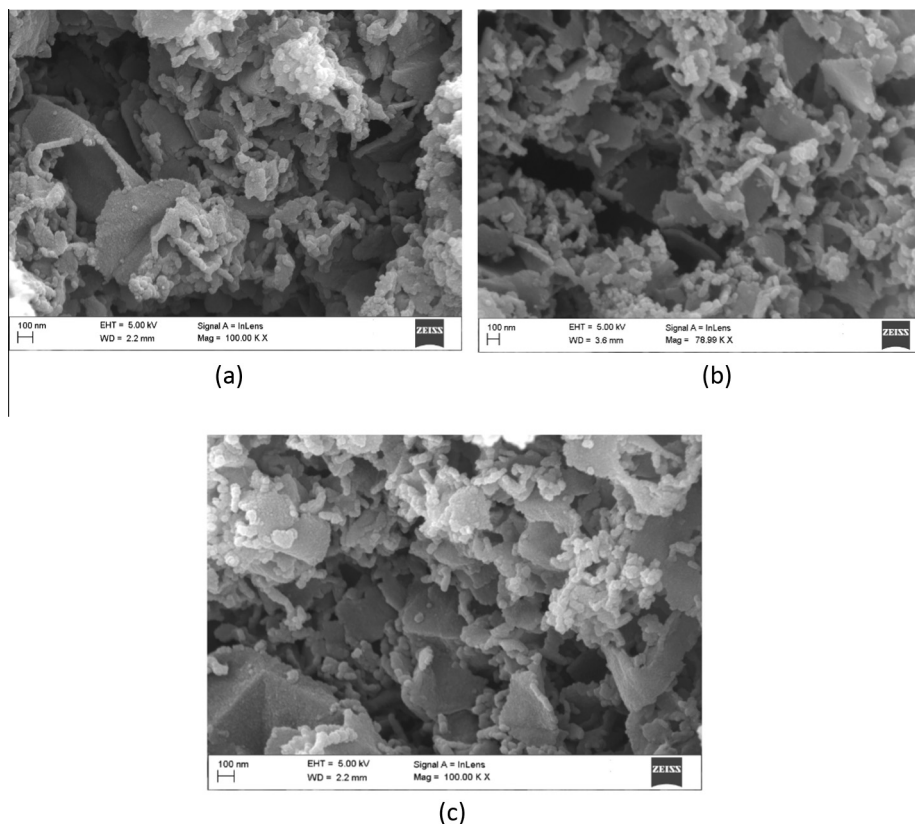


**Figure 9** Possible mechanism of few-layered graphene formation via ECE of ZCB.

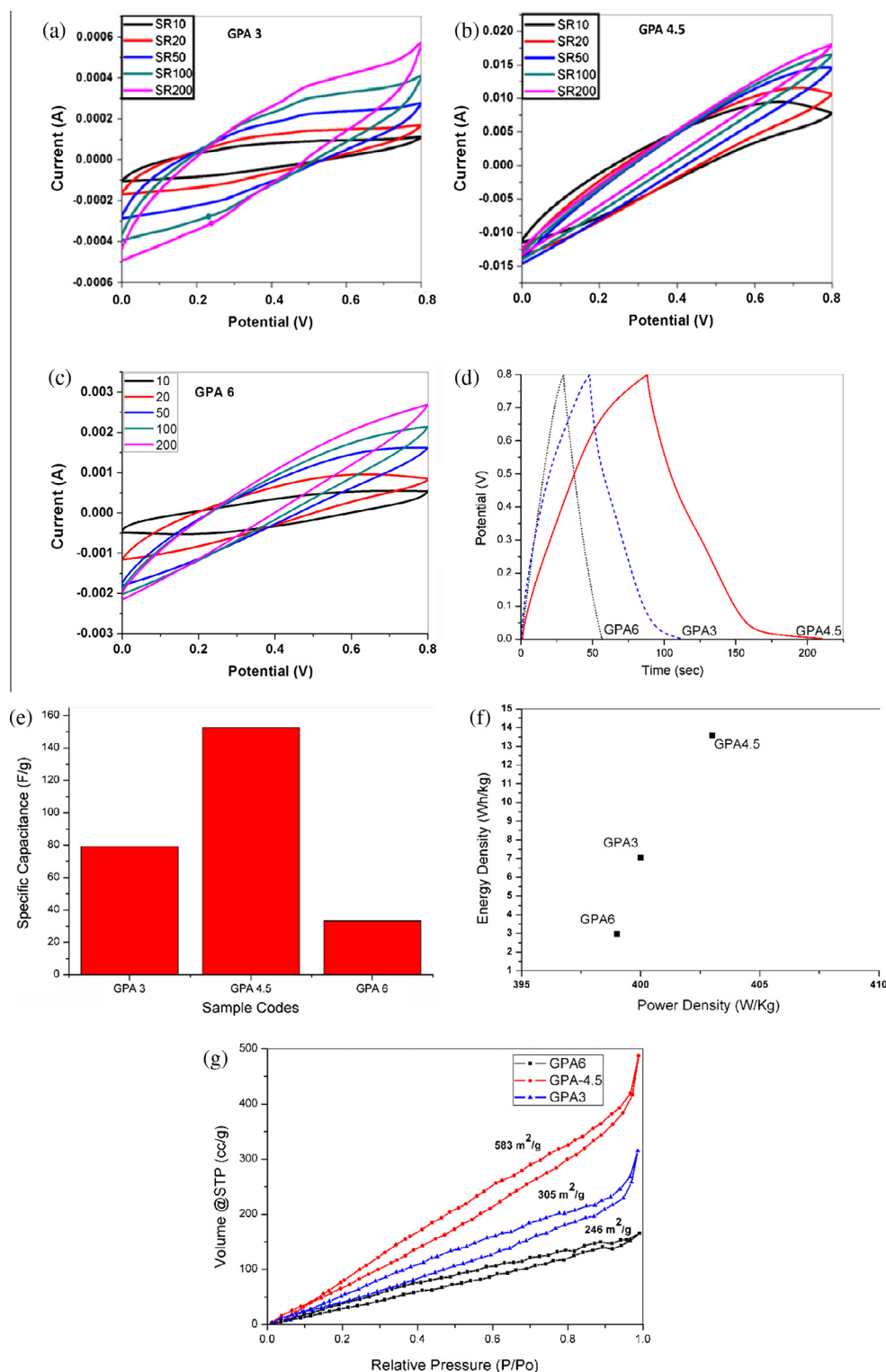
molecule in water and probable mechanism of intercalation is shown in Figs. 8 and 9, respectively.

### 3.3. Application of synthesized graphene for supercapacitor electrodes

To access the applicability of our prepared graphene, for supercapacitor electrode, we have synthesized three polyaniline (PANI) based binary nanocomposites (GPA3, GPA4.5 and GPA6 with 3 V, 4.5 V and 6 V samples, respectively) using reported synthetic route (Dong et al., 2012). To confirm the coating of PANI, over graphene sheets, FESEM analysis was carried out and is shown in Fig. 10. From the FESEM images it is clear that all the sheets were coated with PANI. In order to evaluate their charge storage performance, electrochemical



**Figure 10** FESEM images of the nanocomposite (a) GPA3, (b) GPA4.5 and (c) GPA6.



**Figure 11** Cyclic voltammograms of (a) GPA3, (b) GPA4.5, (c) GPA6, (d) Charging/discharging behavior, (e) Specific Capacitance, (f) Ragone Plot and (g) BET surface area of all three nanocomposites.

analysis was carried out and results are discussed in the following section.

The cyclic voltammograms (CV) of all nanocomposites at various scan rates (SR) of 10, 20, 50, 100 and 200 mV/S in the potential range of 0–0.8 V are shown in Fig. 11(a–c). As

can be seen from the CVs of all nanocomposites, with the increase in scan rate the current also increases which can be attributed to the diffusion kinetics (Dong et al., 2012; Basnayaka et al., 2013). For a fixed potential window, slower scan rate will take longer to record a voltammogram as com-



pared to fast scan rate which in turn alter the size of the diffusion layer above the electrode surface. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison with a fast scan rate and hence the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux toward the electrode the magnitude of the current will be lower at slow scan rates and higher at high rates. In addition, during the potentiodynamic investigation there was no clear redox pairs that were found on both positive and negative sweep. This could be ascribed to the dominating factor of scan rate. At higher scan rates electrolyte does not get sufficient time to access the inner active electrode surface and as a result no redox point is achieved. Thus in our case at every scan rate, from 10 mV/s to 200 mV/s, no clear redox pairs were found in the nanocomposites (Dong et al., 2012; Basnayaka et al., 2013; Wang et al., 2012). Further, galvanostatic charging/discharging of as prepared graphene based nanocomposites, at a current density of 1 A/g, was performed and is presented in Fig. 11(d). It was observed that discharge time of GPA4.5 is higher than that of GPA3 and GPA6 which indicates a higher specific capacitance of GPA4.5. The higher discharge time for nanocomposite GPA4.5 could be ascribed to the combined electrochemical double layer capacitance and pseudocapacitance from graphene and PANI, respectively (Basnayaka et al., 2013; Wang et al., 2012). Specific capacitance (SC), energy density (ED) and power density (PD) were calculated from galvanostatic charging/discharging plots to investigate the electrochemical performance of as synthesized nanocomposites using the following formulas and bar plot of SC along with ragone plot is shown in Fig. 11(e and f):

$$\text{Specific capacitance} = I\Delta t/m\Delta V,$$

where  $I$  (A) = Current,  $\Delta t$  (s) = Discharging time,  $m$  (g) = mass of active material and  $\Delta V$  (V) = Potential Window.

$$\text{Energy density} = CV^2/2(\text{W h/kg})$$

where  $C$  = Specific Capacitance,  $V$  = Potential window

$$\text{Power density} = E/\Delta t(\text{W/kg})$$

where  $E$  = Energy density,  $\Delta t$  = Discharge time

The results suggest that, GPA4.5 possessed the maximum specific capacitance of 151 F/g as compared to GPA3 and GPA6 which possess only 78 F/g and 33 F/g, respectively (Fig. 11(e)). This specific capacitance of GPA4.5 is higher than similar reported works where graphene based supercapacitors showed a specific capacitance of 117 F/g in aqueous H<sub>2</sub>SO<sub>4</sub> and 135 F/g in aqueous electrolyte (Basnayaka et al., 2013; Wang et al., 2012). Similar trend was also observed for ED and PD, where GPA4.5 showed maximum value with respect to other studied nanocomposites (Fig. 11(f)). Further the enhanced specific capacitance of nanocomposite GPA4.5 could be ascribed to the higher surface area of GPA4.5 as compared to other studied systems. To confirm this we have measured the BET surface areas of all 3 nanocomposites by QUANTOCHROME NOVA WIN surface area analyzer and are presented in Fig. 11(g). It was found that GPA4.5 possessed a BET surface area of 583 m<sup>2</sup>/g against 305 and 246 m<sup>2</sup>/g for GPA3 and GPA6, respectively. This suggest that GPA4.5 has higher surface area as compared to GPA3 and GPA 6 which can be attributed to better exfoliation of graphitic layers at 4.5 V and subsequent coating of PANI. During composite

fabrication these graphene sheets act as a template for the deposition of PANI leading to high surface area (Basnayaka et al., 2013; Dong et al., 2012; Wang et al., 2012). In case of GPA4.5 graphene sheets are uniformly coated by PANI resulting in enhanced electroactive surface area thus consequently increasing the double layered capacitance and hence the specific capacitance. However, in GPA3 and GPA6 low electroactive surface area, even after the deposition of PANI, leads to lower specific capacitance.

#### 4. Conclusion

A facile synthesis process was developed for the preparation of few layered graphene from waste zinc carbon battery electrode. It was found that 4.5 V is the optimum voltage which produced good quality graphene. The FESEM, Raman analysis and powder XRD confirmed this observation. The application of these graphene was explored for supercapacitor electrode and it was found that in combination with polyaniline 4.5 V sample produced maximum specific capacitance.

#### Acknowledgments

We acknowledge Dr. VasantSathe (Scientist F) of UGC-DAE Consortium for Scientific Research, Indore for the help with micro-Raman measurements. We are also grateful for financial support from ISM Dhanbad and DST (Grant Number: SERB/F/4910/2013-14) and NCN Grant No. 2012/05/B/ST5/00709.

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