Simple and cost-effective synthesis of activated carbon@few layers of graphene composite electrode for supercapacitor applications

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Abstract. We report a simple and low-cost technique to prepare a composite comprising of activated carbon and few layers of graphene sheets and fabricated as electrode material for supercapacitor (SC) applications. The composite is characterised by using Raman spectroscopy, powder X-ray diffraction (XRD), scanning electron microscope (SEM) and current-voltage (I-V) measurements. The synthesized composite is investigated by using galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) measurements in 3M KOH aqueous electrolyte to evaluate its electrochemical performance. The composite results high specific capacitance from 173 to 564 F/g at different scan rates (100-5 mV/s), analysed by CV and the capacitances resulted in GCD measurement were 196 to 587 F/g at various current densities (5-1 A/g). The cycle stability of the as-prepared AC/graphene composite is also tested and observed that 89% of capacitance is retained even after 5000 cycles which reveals the excellent long term charge-discharge stability of the prepared composite. Therefore, the composite performs very well in storage as well as life cycling. The obtained results suggest that AC/graphene composite can be a suitable electrode material for high-performance SC.

Keywords: Activated carbon, graphene, cyclic voltammetry, supercapacitor, scanning electron microscope

1. Introduction

The enormous population growth and development of portable electronic devices, a novel storage device with high energy and power efficient is the crucial demand. Supercapacitors (SCs) are the electric double-layer capacitor (EDLC), that bridges the gap between conventional batteries and traditional dielectric capacitors in terms of power/energy. It has high power density, fast charge/discharge rate, low equivalent series resistance, operation in extended temperature range and long cycle life (> 100000 cycles) that are essential for practical applications [1-5]. Therefore, SC has potential applications such as in industrial power supplies, hybrid electric vehicles, consumer electronics and memory back-up systems. However, the SC fall behind in many potential applications due to its significantly low energy density. Therefore, enhancement of energy short of dropping its power density for SC device is the most important challenge for the researcher now a day. People have given many efforts to design the SC devices taking various electrode materials to enhance the overall energy and power performance. SCs devices fabricated by carbon-based electroactive materials, metal oxide/hydroxide and electrochemical
conducting polymers [6] are being investigated extensively. Although low cost, ease of fabrication, high capacitance and good conductivity have the advantages of electrochemical conducting polymers, however, they have very poor cycle life and relatively low mechanical stability. Similarly, metal oxide/hydroxide based single electrode pseudocapacitor show improved capacitance as well as energy performance, however, high materials fabrication cost, poor conductivity and degradation of the materials during redox chemical reaction are the serious concern. This limits the applications of oxide/hydroxide based pseudocapacitor in practical applications. On the other hand, carbon-based materials including carbon nanotubes [7, 8], activated carbon [9-11] and graphene [12-18] are being mostly used in EDLC because of their outstanding physical and chemical properties. Among various carbon materials, activated carbon (AC) is widely used as promising electrode material in SCs due to its large specific surface area around 500-3500 m²/g, high packing density and cost-efficient. Nevertheless, the commercial application of AC limited to only small markets due to their poor electrical conductivity and low mesoporosity which produces a long diffusion pathway for ions which results in limited energy storage as well as very low rate capability. These drawbacks make AC unfavourable for the excellent cycleability and process of rapid charge/discharge. So controlling narrow pore size distribution and increasing electrical conductivity without losing packing density and surface area are still challenging for AC.

Due to its excellent chemical stability, high surface area (2675 m²/g), the high theoretical value of specific capacitance (up to ~ 550 F/g), good thermal and electrical properties, graphene has been given special attention towards SCs. However, experimentally the intrinsic capacitance (21 μF) of graphene was far away from the theoretical value [19]. Many efforts have been made to enhance the capacitance of SC based on modified graphene and graphene [20-22]. Unfortunately, based on graphene the experimentally obtained specific capacitance value far lower than the theoretical one due to the unavoidable tendency of graphene sheets to form restacking of layers during the preparation and consequent production processes that result in loss of their surface area and hence only the bottom and the top surface of graphene can accumulate electrolyte ions, which results into lower the capacitance as the area of the stacked surface of graphene could not be used [23]. The low packing density i.e. 0.005 g cm⁻³ is one more limitation of graphene that affect the volumetric capacitance of electrode materials. Also, due to its exceptional sheet-like morphology simultaneously achieving high surface area and volumetric density is very difficult for graphene. Therefore, enhancement of packing density without losing a surface area of graphene is highly necessary and imperious. However, the restacking tendency and low packing density of graphene could be overcome by integrating with AC and simultaneously the electrical conducting nature of AC could be enhanced and hence, better storage performance can be achieved in the composite electrode. Zheng et al. have prepared porous graphene/activated carbon composite where they found a maximum capacitance of 210 F/g and 103 F/g in aqueous electrolyte and organic electrolyte [24]. Chen et al. have prepared graphene–activated carbon composite by chemical activation and found maximum specific capacitance 122 F/g in an aqueous electrolyte [25]. Yu et al. have synthesized KOH activated carbon/graphene nanosheets composites and they have found maximum capacitance of 173 F/g and 205 F/g in organic and aqueous electrolyte [26].

Taking motivation of above reports, herein we have prepared AC/few layers of graphene (graphene) composite in a low cost as well as a simple method and achieved good cycle stability and the enriched storage performance for SCs electrode. Here graphene is being prepared using an electrochemical method where the few layers of graphene are achieved with mass scale and integrated with host AC, to be used in SC for commercial applications. By incorporating graphene over host AC, which not only increases the packing density but also avoids the restacking of graphene sheets by acting AC as a spacer between the sheets. Similarly, introducing graphene in host AC will especially increase the conductivity and reduces the long diffusion pathway of AC significantly. Moreover, the aqueous electrolyte has been used to get better cycle stability of AC/graphene composite electrode. The composite gives a specific capacitance of 564 F/g at 5 mV/s from CV and 536 F/g at 1 A/g from GCD in 3M KOH aqueous electrolyte.
electrolyte. Therefore, the finding results claim that synthesized composite can be a suitable electrode material for SC devices.

2. Experimental

2.1 Used chemicals

The chemicals have been used without any further purifying. High-quality chemicals like nitric acid (HNO₃ with > 98% purity), oxalic acid (> 99 % purity) and graphite rods are procured from Sigma-Aldrich (India).

2.2 Synthesis of AC/graphene composite

Graphene has been prepared by the electrochemical method [27] in which the interaction between graphite rods and oxalic acid take place. The good quality of few layers of graphene sheets has been recovered after sonicating and filtering several times. Commercially available AC has been used after treating with HNO₃ for surface modification and to increase its porosity for better ions accumulation [28]. AC/graphene composite has been prepared by the sonication of AC and graphene individually for 3 hours to get the uniform dispersion. Then a mixture of AC and graphene (4:1 weight ratio) put into magnetic stirring for 12 hours at room temperature. Then using 100 mL of Teflon-line autoclave the mixture was closed and kept at 180°C for 12 hours. The AC/graphene composite was obtained after drying in a muffle furnace at 110°C for 24 hours.

2.3 Electrode fabrication

Three electrode set-up has been used where synthesized AC/graphene composite act as working electrode, the platinum wire is used as counter electrode and Ag/AgCl as a reference electrode in 3M KOH aqueous electrolyte for the electrochemical analysis of prepared composite. The working electrode was prepared as follows: at first AC/graphene was added with Nafion binder and carbon black in 8:1:1 weight ratio (to form a slurry) and the slurry (1mg) of prepared AC/graphene composite with carbon black and Nafion binder was pressed on Ni-foam of dimension 10mm ×10mm× 1mm and dried at 60°C for 24 hours using the vacuum. Then the AC/graphene composite was investigated in an electrochemical workstation using both CV and GCD measurements.

3. Results and discussions

The microstructure of prepared AC/graphene composite, as well as AC and graphene, is characterised by using SEM shown in figure 1. AC shows a large number of interconnected pores and these pores are accumulating the electrolyte ions at the electrode surface (figure 1 (a)). Graphene shows that the layers are well exfoliated with orienting randomly and showing agglomeration of layers (figure 1(b)). Figure 1 (c) confirm that the graphene is well distributed over AC and some of the AC are found to be distributed in between the graphene layers.

![Figure 1](image-url)

**Figure 1.** Surface morphology of (a) AC, (b) graphene and (c) AC/graphene composite.
The phase formation of synthesised materials such as AC, graphene and AC/graphene composite is characterised by using XRD shown in figure 2 (a). AC shows two broad peaks at $2\theta = 23.7^\circ$ and $43.5^\circ$ with (002) and (101) plane which indicates that the graphite crystallite is present and also, confirm the commercial AC [29]. Graphene gives a very sharp peak at $2\theta = 26.78^\circ$ with (002) plane results in the presence of graphite crystallite with large crystallite size and also confirms the hexagonal structure. Two peaks at $2\theta = 26.34^\circ$ and $42.41^\circ$ with (002) and (101) plane are found for AC/graphene composite where the peak at (002) plane is sharper i.e. less broadening than AC which reveals that the crystallite size increases in composite and further, reveals the presence of graphene in AC.

Raman spectroscopy study is very much essential to investigate the presence of structural defects and materials purity. Hence, the Raman spectra of AC/graphene composite, host AC and graphene have been shown in figure 2 (b). Two characteristics bands i.e. D (defect band) at $\sim 1334$ cm$^{-1}$ and G (carbon band) at $\sim 1583$ cm$^{-1}$ have been found for AC. Similarly, for graphene two bands i.e. D at $\sim 1351$ cm$^{-1}$, G at $\sim 1587$ cm$^{-1}$ and the composite gives D at $\sim 1353$ cm$^{-1}$, G at $\sim 1592$ cm$^{-1}$. It has been found that by incorporating graphene on AC, both D and G peaks were slightly shifted towards the right probably due to the motion of carbon atoms in graphite layers. The ratio of D and G intensity ($I_D/I_G$) gives the materials purity and amount of structural defects. Lower the ($I_D/I_G$) ratio higher will be the purity of the material and less will be structural defects and vice-versa. The calculated ($I_D/I_G$) ratios for AC, graphene and AC/graphene composite are 1.06, 0.93 and 1.01. Therefore, by introducing graphene on AC the materials purity increases and structural defects decrease in the composite.

![Figure 2](image-url)

**Figure 2.** (a) XRD pattern and (b) Raman spectra of AC, graphene and AC/graphene composite.

Figure 3 shows the change in current at various applied voltage of AC/graphene composite, AC and graphene with a maximum applied voltage of 7V. AC shows the linear change of current with applied voltage. It is observed that the I-V curve of AC looks like the current is not changing with applied voltage owing to a low current of AC i.e. 0.07mA at 7V compared to graphene and AC/graphene composite. Graphene shows Ohmic behaviour i.e. current changes linearly with voltage and the maximum current was 3.61mA at 7V. It has been found that AC/graphene composite gives a maximum...
current of 1.65mA at 7V. Therefore, by incorporating graphene on host AC the increase in current in AC is observed due to the highly conducting nature of graphene that results in an increase in the rate of ions transfer within the composite electrode.

The cell configuration in an electrochemical measurement acts a vital role to quantify the exact capacitance of electrode material for SCs application. Two electrode set-up gives more accurate results compared to three electrodes for asymmetric SC devices [30, 31]. However, we have studied in three-electrode set-up by using both CV and GCD in 3M KOH aqueous solution. Both CV and GCD have been used to evaluate the specific capacitance of prepared composite using Eq. (1, 2).

\[
C_{sp} = \frac{AI}{2\Delta V \frac{dv}{dt} m}
\]

\[
C_{sp} = \frac{I\Delta t}{m\Delta V}
\]

where \(AI\) is the total area under CV curve in one cycle (AV), \(dv/dt\) is the scan rate (mV/s), \(C_{sp}\) is the specific capacitance (F/g) obtained from CV and GCD, \(\Delta V\) is the potential window (V), \(\Delta t\) is the discharge time (S), \(m\) is the loading mass of material (mg), and \(I\) is the current density (A/g).

The CV images of AC, graphene and prepared AC/graphene composite at 5 mA/s in 3M KOH solution is shown in figure 4 (a) and the composite gives the CV curve with a large integrated area than the precursors (AC and graphene) which indicates the storage capacity of synthesised AC/graphene composite is decent. The CV curves of AC/graphene composite at different scan rate from 5 to 100 mA/s with a potential range within -0.1 to 0.6V is shown in figure 4 (b) and as the scan rate increases, the integrated area under the curve found to be increased which indicates the outstanding charge storage capacity of the composite [32]. Also, it has been found that the shape of CV images of the composite at
various scan rate does not change when increasing the scan rate which confirms the fast transfer of charge takes place inside the AC/graphene electrode [33]. The CV curves of prepared composite demonstrate tends to rectangular shape (as expected for EDLC behaviour in carbon materials) without any redox peak is another indication of good storage behaviour of AC/graphene composite.

![Figure 4. (a) CV images of AC, graphene and AC/graphene composite at scan rate of 5 mV/s, (b) CV images of AC/graphene composite at various scan rate (5-100 mV/s), (c) GCD images of AC/graphene composite at different current densities (1-5 A/g), and (d) Cycle stability of AC/graphene composite over 5000 cycles.]

The composite has resulted in enhanced capacitances i.e. 564, 473, 377, 291, 215 and 173 F/g at 5, 10, 20, 40, 80 and 100 mV/s which were evaluated taking Eq. (1) from the CV. Hence, the maximum capacitance of 564 F/g at 5 mV/s is obtained for composite which is higher compare to AC (349 F/g) and graphene (296 F/g). The composite electrode showed enhanced capacitance compared to precursors owing to the incorporation of highly conducting graphene, which increases the rate of ions transfer and presence AC provides more packing density and surface area within the composite. GCD measurement has been performed to quantify the consistency of capacitance of AC/graphene composite obtained as of CV with the capacitance obtained from GCD. Figure 4 (c) shows the GCD curves of AC/graphene composite at a different current density from 1 to 5 A/g and the obtained curves are triangular shape as expected for EDLC behaviour. The capacitances obtained from GCD measurement were 587, 483, 379, 345 and 314 F/g at 1, 2, 3, 4 and 5 A/g, evaluated using Eq. (2). So the highest capacitance achieved as of the GCD is 587 F/g at 1 A/g and the obtained capacitances from GCD are consistency with CV which
also reveals that the composite electrode performs excellently in terms of energy storage. The long-term cyclic performance of synthesised composite was demonstrated as shown in figure 4 (d) and 89% of capacitance is retained over 5000 cycles at 1 A/g that indicates the outstanding cycle stability of the AC/graphene electrode. Also, the composite performs very well in terms of storage and stability owing to the presence of aqueous electrolytes where more number of ions of aqueous electrolytes are able to access the electrode materials due to the compatibility of pore size of electrode material and ions size of aqueous electrolytes.

Figure 5. (a) Specific capacitance of AC/graphene composite at various scan rates and (b) Specific capacitance of AC/graphene composite at different current densities.

The change in specific capacitance at various scan rates of the AC/graphene composite shown in figure 5 (a) and observed that the capacitance gradually reduces as the scan rate increased probably owing to the deficiency of time to enter the small pores of electrode materials by the electrolyte ions and that results into lower specific capacitance at high scan rate [34]. Figure 5 (b) shows the deviation of capacitance at different current densities and found that capacitance decreases with increasing current density because at high current density very few electrolyte ions able to pass the electrode material.

4. Conclusions

AC/graphene composite is being prepared successfully in a low-cost as well as a simple method and the synthesised composite was investigated by using CV and GCD in 3M KOH solution in 3 electrode set-up. The composite showed the enhanced capacitance of 564 F/g at 5 mV/s and 173 F/g at 100 mV/s form CV. Also, using GCD the highest capacitance achieved by the composite was 587 F/g at 1 A/g and the obtained capacitances from GCD were reliability with the CV results which reveals the excellent charge storage capacity of AC/graphene composite. The large capacitance has been found in the composite electrode due to the presence of highly conducting graphene provide fast ions transfer and the addition of AC offers large packing density within the AC/graphene composite electrode. Also, the long terms cycling performance of synthesised composite was demonstrated and 89% of capacitance is retained over 5000 cycles at 1 A/g. Hence, the AC/graphene composite not only gives good cycle stability but also provide enhanced storage performance and can be a suitable electrode material for SC application.

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