Short communication

# Graphene oxide – Polyvinyl alcohol nanocomposite based electrode material for supercapacitors

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## HIGHLIGHTS

- GOPVA nanocomposite an environment friendly organic electrode material.
- Have high specific capacity amongst most carbon based electrode materials.
- Can sustain high specific capacitance over long charging and discharging cycles.
- Have low internal resistance.

## ARTICLE INFO

## ABSTRACT

Supercapacitors are high capacitive energy storage devices and find applications where rapid bursts of power are required. Thus materials offering high specific capacitance are of fundamental interest in development of these electrochemical devices. Graphene oxide based nanocomposites are mechanically robust and have interesting electronic properties. These form potential electrode materials efficient for charge storage in supercapacitors. In this perspective, we investigate low cost graphene oxide based nanocomposites as electrode material for supercapacitor. Nanocomposites of graphene oxide and polyvinyl alcohol were synthesized in solution phase by integrating graphene oxide as filler in polyvinyl alcohol matrix. Structural and optical characterizations suggest the formation of graphene oxide and polyvinyl alcohol nanocomposites. These nanocomposites were found to have high specific capacitance, were cyclable, ecofriendly and economical. Our studies suggest that nanocomposites prepared by adding 0.5% wt/wt of graphene oxide in polyvinyl alcohol can be used an efficient electrode material for supercapacitors.

Carbon has emerged as the wonder element of the decade and its use in different allotropic forms has initiated a lot of research activity in the development of various types of devices including batteries, electronic devices etc. Carbon based materials are not only environment friendly, economical, easy to process but also exhibit a wide range of properties. The use of carbon based materials in supercapacitors has been second to none. Several carbon based materials such as activated carbon (AC), mesoporous carbon (MC) [1], carbon nanotubes (CNTs) and graphene have been explored for fabricating supercapacitor electrodes to enhance charge storage and performance of these devices. Even though these materials as electrodes display good stability, their capacitive

values are limited. Several combination of materials such as carbon nanoparticles/$MnO_2$ nanorods hybrid structure [2], graphene oxide (GO) supported by needle like $MnO_2$ crystals [3], pristine and chemically modified graphene and polyaniline (PANI) nanofiber composites [4], PVP-graphene composites [5], graphene sheet wrapped polyaniline nanowire arrays on nitrogen-doped carbon fiber cloth (eCFC) [6], and graphene-iron nanocomposites [7] have been studied as electrode materials. Several problems associated with these include environmental issues during disposal, cyclability, stability, swelling etc. GO is expected to provide pseudo-capacitance effects due to attached oxygen-containing functional groups on its basal planes [8]. Furthermore GOPVA nanocomposites have been recently reported to have excellent mechanical properties [9–12]. Thus nanocomposites of GOPVA form material of choice for investigation of electrochemical activity. This has motivated synthesis of oxidized graphene based nanocomposites to

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exploit the exotic properties of graphene based materials and the host matrix to provide large surface area and large number of pseudo charge storage centers. Here we propose the use of GO as a filler in polyvinyl alcohol (PVA) matrix as an electrode material for supercapacitors. GO is expected to assist the charge storage using electric double layer capacitance (EDLC) while PVA assists in charge storage by providing pseudocapacitive nature using redox reaction. GO can be synthesized economically and PVA is one of the readily available green polymers, to synthesize these eco-friendly nano-composites for supercapacitor electrodes. Functional groups present in GO act as effective means for improving the dispersion and interfacial bonding with the PVA matrix leading to better homogenization when formed a composite as compared to graphene. At the same time PVA has good binding capacity to GO with better processability for making devices. We have synthesized several compositions of nanocomposites using GO and PVA in solution phase. Electrochemical characterizations suggest that 0.5 wt% of GO in PVA matrix (referred to as GOPVA in the manuscript unless otherwise stated) shows specific capacitance of >400 F/g, is cyclable and can be used as an efficient electrode material in a supercapacitor.

GO was synthesized using an ecofriendly improved synthesis method. The synthesis process is briefly discussed here. 3.0 gm of graphite flakes >99% purity was added to 9:1 mixture of concentrated $H_2SO_4$:$H_3PO_4$ under vigorous stirring. $KMnO_4$ (18.0 g) is added slowly. The reaction was then heated to 50 °C and stirred approximately for 12 h and subsequently cooled to room temperature and finally put into an ice bath. Addition of water (400 mL) with 30% $H_2O_2$ (3 mL) turned the color of the solution from dark brown to yellow. The mixture was then filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions and then sonicated for 30 min to exfoliate it. Several compositions of composites were prepared by mixing different amount of GO solution into PVA solution in water. This mixing of GO filler at molecular level is expected to provide maximal mechanical enhancement resulting in synthesis of a high performance nanocomposites. Nanocomposite prepared by adding aqueous solution of 200 mg PVA to 1 mg GO 0.5% wt/wt suspension in water corresponding to 0.5 wt% was labeled as GOPVA 200. Nanocomposites with 1% wt/wt, 0.66% wt/wt, 0.58% wt/wt, 0.52% wt/wt, 0.50% wt/wt, 0.45% wt/wt and 0.4% wt/wt of GO in PVA labeled as GOPVA100, GOPVA150, GOPVA170, GOPVA190, GOPVA200, GOPVA220 and GOPVA250 were synthesized and characterized. The acronym GOPVA has used to represent GOPVA200 in rest of this manuscript unless specified otherwise.

The GOPVA samples were characterized using X-Ray diffraction, UV–Vis absorption and Raman spectroscopy. Microstructural information was obtained using Raman imaging technique. The nanocomposite samples were characterized electrochemically using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Working electrode for electrochemical characterization was prepared by pouring above solution drop by drop on graphite electrode and dried under room temperature.

Structural characterization using X-Ray diffraction was performed to confirm that the material synthesized was nanocomposite and not a blend. The XRD pattern of exfoliated GO film exhibits diffraction peak at $2\theta \sim 9.3°$ and $\sim 18.7°$, while pure PVA shows diffraction peak at $2\theta \sim 19.6°$ resulting from the (101) crystal planes as shown in Fig. 1(a). The X-ray diffraction pattern of GOPVA200 nano composite in Fig. 1(a) shows a peak at $2\theta \sim 19.6°$ suggesting that GO was exfoliated and dispersed into the PVA matrix. Both these values are in good agreement with reported data on GO and PVA [9,13]. Since this diffraction peak in GOPVA is very broad and overlaps the region of diffraction peak of GO at $2\theta \sim 18.7°$, a need was felt to characterize the samples further using optical spectroscopy.

The samples were characterized using Raman and UV–Vis absorption spectroscopy to reinforce our conclusion that the synthesized material was a nanocomposite and not a blend. The normalized absorption spectra of materials performed in aqueous dispersions is shown in Fig. 1(b). GO samples show a major absorption peak at ~232 nm which can be attributed to л → л* transition, while the shoulder peak at ~300 nm originates from n → л* due to the presence of different oxygen functional groups present in graphene oxide [13]. The broad peak in the ultraviolet absorption of PVA ~265−280 nm is consistent with the signatures attributed to carbonyl containing segments of the form −(CH= CH)$_2$ CO− and an indicative of conjugated double bonds of polyenes [14]. The broadened peak enveloping the GO and PVA peaks suggest the presence of both the components in the nanocomposite.

Raman spectra of the samples shown in Fig. 1(c) were obtained by depositing the samples on a glass substrate. The Raman spectrum of GO is characterized by two main features at 1591 cm$^{-1}$ and ~1347 cm$^{-1}$ representing the G and D bands respectively [15]. Besides, showing Raman activity at wave numbers smaller than 2000 cm$^{-1}$ (not shown in data), PVA shows most prominent Raman peak at ~2924 (5) cm$^{-1}$ arising due to the valence C−H vibrations. This is in good agreement with the reported data [16]. The Raman signature of the composite shows the features of both GO and PVA distinctly suggesting the synthesis of GOPVA nanocomposite.

Raman mapping was performed on the GOPVA samples. The sample was scanned for the 'D' and 'G' band of GO and the 2924 cm$^{-1}$ band of PVA shown in Fig. 2(a–c). Fig. 2(d) shows combined image for all the three scanned frequencies at 1347 cm$^{-1}$, 1591 cm$^{-1}$ and 2924 cm$^{-1}$ suggesting uniform distribution of the GO in PVA matrix. Cross-sectional micrographs obtained using FEGSEM as shown in Fig. 2(e) and (f) suggest that GO-PVA films are of better as compared to pure GO films respectively.

To explore the possibility of using GOPVA nanocomposite as an electrode material, samples were characterized using cyclic-voltammetry (CV), electrochemical impedance spectroscopy (EIS). The pseudo-capacitive nature of the GOPVA nanocomposite was investigated using CV. A traditional three electrode system was used in which Teflon coated graphite, GOPVA and standard calomel was used as the counter, working and reference electrode respectively. The electrolyte chosen was 46 mM aqueous solution of sodium-sulphate. Cyclic voltammetry was carried out in the voltage window of 0 V−1 V with a scan rate 10 mV/s. The CV of GOPVA samples in Fig. 3(a) shows cyclic voltammogram of GO, PVA and GOPVA nanocomposite. Even though the specific capacitance of PVA is very small ~27 F/g, the specific capacitance estimated from CV curves suggest that addition of PVA increases the specific capacitance from ~244 F/g (pure GO) to ~400 F/g (GOPVA nanocomposite) at scan rate of 10 mV/s. GOPVA has higher specific capacitance than many other reported carbon based materials such as nanoporous carbon (240 F/g) [17], activated carbon fibers (60 F/g) [18], activated carbon and carbon nanotube mixture (90 F/g) [19], Functionalized graphene sheets (230 F/g) [20]. The enhanced capacitive nature of GO-PVA nanocomposites can be understood in terms of interaction of the −OH groups in PVA with carbonyl and hydroxyl groups in GO. This interlinking in GO/PVA is understood to enhance the value of $\varepsilon$ which attributes to increase in the value of conductivity and electrode polarization Further presence of GO helps in preventing the cross linking between PVA chains. As GO and PVA have interaction between their oxygen functional groups. Both components are water soluble so the internal resistance gets reduced with aqueous electrolyte. Further, the GOPVA nanocomposites are very stable and were found to retain ~92% of its specific capacitance even after 400 cycles. The CV curve of graphene oxide in Fig. 3(a) shows a broadened peak suggesting the presence