Flexible Fibre Supercapacitor using Synthesized Biomass based Activated Carbon and Few Layer Graphene for Wearable Electronic Devices

Ankit Singh¹, Kaushik Ghosh², Sushil Kumar², Ashwini K. Agrawal³, Manjeet Jassal³, Pranab Goswami¹, Harsh Chaturvedi^{1*}

¹Centre for Energy, Indian Institute of Technology Guwahati

²Institute of Nano Science and Technology, Mohali

³SMITA research lab, Indian Institute of Technology Delhi

harshc@iitg.ac.in

Abstract. We have fabricated a flexible fibre supercapacitor having twisted architecture incorporating synthesized carbonaceous electrode materials from widely available inexpensive biomass (banana peel) for energy storage which can be utilized for powering emerging wearable electronic textiles and devices. Activated carbon and few layer graphene were synthesized by carbonizing KOH impregnated and ethanol/acetone washed banana peels respectively at high temperature under inert atmosphere. The synthesized carbonaceous electrode materials along with TiO₂ nanopowder were deposited on conductive carbon fibre followed by dip coating with gel electrolyte and twisting to develop the supercapacitor. The fabricated fibre supercapacitor demonstrated high specific capacitance of 15.45 F/g and volumetric capacitance of 1.77 F/cm³ at 10mV/s scan rate. The developed supercapacitor retained ~92% of capacitance upon bending. The fibre supercapacitor can be fabricated on large scale using simple methods and inexpensive biomass for powering wearable electronic applications.

Keywords: Flexible, Fibre Supercapacitor, Inexpensive Biomass

1 Introduction

Recent progress in wearable electronics has affirmed its promising future. The key challenge inhibiting its wider acceptance is lack of wearable energy storage device. Supercapacitor has long life, is safe and environmentally friendly and can prove to be a good alternative for wearable energy storage applications. [1] Fibre supercapacitor exhibit unique advantages as compared to existing solid-state planar supercapacitor in terms of energy density, flexibility, lightweight, varied architecture and applications. [2,3] We demonstrate fibre supercapacitor having a twisted architecture with asym-

metric electrode configuration, using conducting carbon fibre incorporated with TiO_2 nanopowder and synthesized biomass based activated carbon and few-layer graphene as active electrode materials. Fibre supercapacitor can be woven into the fabric for flexible/wearable energy storage hence eliminating the requirement of carrying bulky devices. This fibre supercapacitor can be utilized in the domain of smart textiles, bio-medical and other wearable electronic applications. [2,3]

2 Experimental

Locally available inexpensive source of biomass like banana peels were washed thoroughly with distilled water and dried at 80°C overnight in vacuum oven which was used for synthesizing activated carbon and few layer graphene.

2.1 Synthesis of Activated Carbon

Fig. 1. : FESEM image of Activated Carbon at (a) 5kX and (b) 10kX magnification showing well porous structure

The dried banana peels were then impregnated with aqueous solution of KOH which was prepared by mixing 3g of KOH flakes with 50ml of DI water for 2 hours. The impregnated peel was dried at 80°C overnight in vacuum oven. The dried impregnated banana peel was carbonized at 600°C for 1 hour inside a muffle furnace in absence of air. The carbonized residue was washed with dilute HCL and DI water until pH 7 was attained and dried at 80°C overnight in vacuum oven resulting in activated carbon. The activated carbon was observed using FESEM as shown in Figure 1 showing its well porous structure. The synthesized activated carbon also has BET surface area of $62.03 \text{ m}^2/\text{g}$. [4]

2.2 Synthesis of few layer graphene

Fig. 2. (a) Raman spectrum of few layer graphene at 633 nm, (b) FESEM image of few layer graphene at 2kX magnification

The dried banana peels were further washed with ethanol/acetone and left to dry at room temperature. The peels were carbonized at 950°C in a tubular furnace for 2 hours in presence of inert argon gas. The carbonized residue was crushed in mortar-pestle resulting in few layer graphene which was verified by Raman spectroscopy (Figure 2(a)) and FESEM investigation (Figure 2(b)). [5]

2.3 Fabrication of fibre supercapacitor

Fig. 3. (a) Schematic representation of twisted fibre supercapacitor, (b) Optical image of fibre supercapacitor fabricated using pair of conductive carbon fibre as substrate, FESEM image of (c) Activated Carbon/Few-Layer graphene at 3kX, Cross-section of silver painted carbon fibres at (d) 250X and (e) 1kX magnification showing individual carbon fibre having an approximate diameter of $7 \mu\text{m}$.

The schematic structure of fabricated twisted fibre supercapacitor is shown in Figure 3(a). A pair of conductive carbon fibre was painted with conductive silver ink (Figure 3(b)) followed by deposition of equal amounts (1mg of each constituent) of TiO_2 / few layer graphene and activated carbon/ few layer graphene (Figure 3(c)) forming the cathode and anode respectively. The Cross-section of silver painted carbon fibres was observed by FESEM at (Figure 3(d)) 250X and (Figure 3(e)) 1kX magnification showing individual carbon fibre having an approximate diameter of $7\mu\text{m}$. The electrodes were dip coated with the PVA/ H_3PO_4 gel electrolyte twice. The gel electrolyte was prepared by mixing 1g of PVA in 10 ml of DI water at 90°C under constant magnetic stirring followed by addition of 1ml of H_3PO_4 acid. [6] The electrodes were twisted and dip coated with the gel electrolyte to have better adhesion and dried overnight at room temperature forming the twisted fibre supercapacitor (Figure 3(b)).

3 Device Characterization

Fig. 4. (a) CV profile at different scan rates, (b) Specific capacitance and Volumetric capacitance plot and (c) CD plots of the fabricated fibre supercapacitor, (d) Supercapacitor retained 92% of capacitance upon bending at 20 mV/s scan rate, (e) Fibre supercapacitor under bent conditions.

The fabricated fibre supercapacitor was characterised by cyclic voltammetry (CV) and charge-discharge (CD) tests by using Metrohm Autolab electrochemical workstation. CV tests were carried out at scan rates ranging from 10 mV/s to 200 mV/s (Figure 4a). From the CV profile, specific capacitance and volumetric capacitance (Figure 4b) were calculated at respective scan rates using formulae,

$$\text{Specific Capacitance (CV curves), } C_{sp} = \frac{A}{m * v * V}$$

$$\text{Volumetric Capacitance (CV curves), } C_v = \frac{A}{\Delta v * v * V}$$

where, A is area of CV curve, m is mass of active electrode material (4mg), Δv is the volume of the device (0.035 cm^3), v is scan rate in mV/s and V is potential window (1V). The fabricated supercapacitor demonstrated specific capacitance of 15.45 F/g and volumetric capacitance of 1.77 F/cm^3 at 10mV/s scan rate. The fabricated supercapacitor was also tested for charge-discharge (CD) at 1mA and 2mA discharge currents (Figure 4c). Specific capacitance and volumetric capacitance were calculated at respective discharge currents using formulae,

$$\text{Specific capacitance (CD profile), } C_s = \frac{I * t_d}{m * V'}$$

$$\text{Volumetric capacitance (CD profile), } C_v = \frac{I * t_d}{\Delta v * V'}$$

where, I is the constant discharge current, t_d is discharge time, m is mass of active electrode material (4mg), Δv is the volume of the device (0.035 cm^3), V' is effective discharge voltage (excluding IR drop). The fabricated supercapacitor demonstrated specific capacitance of 1.27 F/g and volumetric capacitance of 145 mF/cm^3 at 2mA (57 mA/cm^3) discharge current. Capacitances of few of the earlier reported twisted fibre supercapacitors are CNT based (13.5 F/cm^3), Graphene based (40 F/g), IR-CNT@PANI electrode (78 F/g) (Table 1&2) [2] and All graphene (GF@3D-G) based ($30\text{-}40 \text{ }\mu\text{F}$ at $2\text{ }\mu\text{A}$), CNT/MnO₂ composite yarn (25.4 F/cm^3 at 10 mV/s), Asymmetric electrodes of Co₃O₄ nanowires and graphene (1.59 F/cm^3 at 40 mA/cm^3) (Table 1) [3]. The fibre supercapacitor retained ~92% of capacitance under bent condition at 20 mV/s scan rate demonstrating its ability for flexible applications (Figure 4(d), (e)). [7]

4 Materials

Titanium(IV) oxide (TiO₂), nanopowder (718467-100G) was obtained from Sigma-Aldrich and has particle size <21nm (TEM). Potassium hydroxide (KOH), flakes

(2815.20.00 – 500G), Orthophosphoric acid (H_3PO_4), 88% (O11329– 500ml), Poly vinyl alcohol (PVA), 98% (3905.30.00– 500G) was obtained from NICE Chemicals Pvt Ltd, Kerala. Silver Ink (200 ml) was obtained from SNAB GRAPHIX (India) Pvt Ltd, Bangalore. Conductive carbon fibres were obtained from SMITA research lab, Textile Department, IIT Delhi.

5 Conclusion

Fibre supercapacitor having twisted architecture was fabricated using synthesized activated carbon and few layer graphene from banana peels along with TiO_2 nanopowder as active electrode materials and conductive carbon fibre as substrate. Porous activated carbon increased the electrode surface area and the few layer graphene increased the conductivity which collectively enhanced the energy storing capability of the fabricated device. The fabricated supercapacitor demonstrated specific capacitance of 15.45 F/g and volumetric capacitance of 1.77 F/cm^3 at 10mV/s scan rate. The twisted supercapacitor also retained ~92% of capacitance upon bending. Other transition metal oxides like MnO_2 , NiO , Co_3O_4 as electrode material should be explored to further increase the energy storing capacity. Coaxial architecture of fibre supercapacitor will further enhance the capacitance and will have better mechanical stability. The fabricated fibre supercapacitor can be used in the domain of smart textiles, biomedical and other wearable electronic applications.

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