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Development and Characterization of Cotton Fibre stabilized MnO_2 decorated Polyaniline hybrid material for Supercapacitor application

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Abstract:

Herein, we report on the development of efficient, sustainable, and environmentally friendly cotton stabilized MnO_2 decorated polyaniline electrode material via facile in-situ approach. Polymerization of aniline was performed in presence of cotton fibre and MnO_2 via chemical oxidative method. Successful formation of hybrid material was confirmed by FT-IR and FESEM analysis. Inherent particle nature of polyaniline was observed to be changed to fibre like morphology due to templating effect of cotton fibre. Electrochemical performances were measured by cyclic voltammetry, charging-discharging and impedance spectroscopy analysis. Presence of cyclic voltammogram, charge-discharge cycles and lower charge transfer resistance of synthesized material demonstrate good electrochemical behaviour for supercapacitor application.

Introduction:

The recent surge of wearable and portable electronic equipment among the public has drawn the attention of the scientific community towards the novel development in this field[1]. The newly developed smart clothing is one of the examples in this prospect. For example, the newly developed smart clothing system which integrate wearable electronics with the everyday clothing system[2]. This type of innovative integrating systems could be used in the various fields such as sports and military equipment's which helping in monitoring as well as communicating, with the personals when it needs[3]. The development of these types of systems always associated with a lot of components such as sensors, well furnished communication system, energy harvesting / energy storing devices, etc. Among this energy harvesting / energy storing device is the crucial part for the functioning of the smart garments[4]. The lighter weight with excellent flexibility of the supercapacitor has outburst the use of conventional power source such as battery or solar powered cells over it in such system. Embedding electrode material over the cotton fabric could help in developing such supercapacitor electrode which performs excellently with retaining the properties of the fabric material[5]. This development could lead to a step towards the smart garments.

There are several reports citing toward the designing of such sustainable electrode for the supercapacitor application. *Zequine et al.* has developed a supercapacitor electrode form the natural fibre obtained bamboo plant[6]. Similarly the α-electrode material developed from the jute fibre has shown the capacitance of 8.65 mF-cm^{-1} at current density 0.1 mA[7]. In another report the supercapacitor developed using cellulose nanofiber is able to light up the LED light for 7s after charging it with 18.7V at 10mA current for 10s[8]. Research has also explored the development of composite electrode materials using natural/ synthetic fibres with some metal oxide for supercapacitor application. *Guo et al.* developed a composite material MnO_2-graphene with synthetic fibre for flexible electrode for supercapacitor[9]. Similarly, a composite of δ-MnO_2 nanorods with soya pod carbon composite shows high charge storage capacity than that of the pristine δ-MnO_2. The developed material is found to retain 91% of the retention in the capacitance even after 6000 charging-discharging cycle[10]. *Özdemir et al.* developed an electrode material by the coting of TiO_2 nanoparticles over the cotton fibre. The TiO_2 decorated cotton fibre not only used as a pH sensor but also shows excellent photocatalytic and antimicrobial activity[11]. In the recent past a composite of Ag-TiO_2 with cotton fibre synthesized by *Aragaez et al.* shows outstanding photocatalytic and antibacterial activity. Although, the metal oxide/ fibre composite based electrode are been explored for supercapacitor and sensor application but metal oxide-polymer-fibre based electrode has been rarely being studied.

In this study we have synthesized a low-cost ecofriendly composite electrode material using conducting polymer- metal oxide and the fabric materials used for clothing using a simple wet chemical method. The as synthesised electrode is subjected to electrochemical analysis which shows an excellent charge storage capacity, and can be used as supercapacitive application.

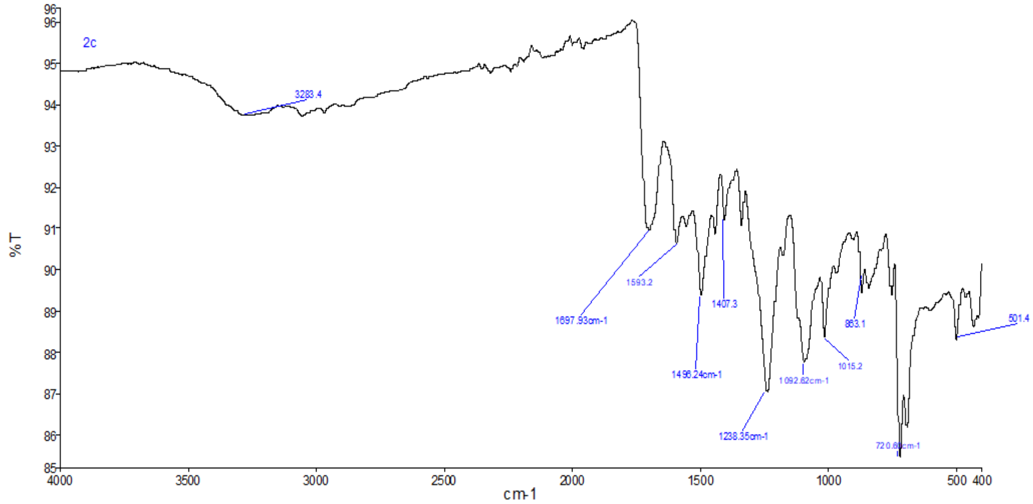
Materials and method:

The monomer of aniline was added to the 1M HCl solution followed by the addition of the metal oxide (MnO_2). The whole reaction step was placed in an ice bath and the temp. of the system was maintained at 0-5^{0}C for 30 minutes to initiation of polymerization. After the complication of the polymerization process cotton fabrics were added to the reaction mixture and allowed to stirrer for few minutes. After the complete mixing of cotton fibre in with the polyaniline (PANI) and MnO_2 to whole step up was placed in a hot air oven at 70^{0}C over night to get PANI-MnO_2@CF electrode material.

The as synthesised PANI-MnO_2@CF electrode was subjected to FTIR for evaluating bonding parameters, FESEM to analyse the surface morphology, Cyclic voltammetry (CV) to study the redox properties galvanostatic charging-discharging to estimate the charging-discharging behaviour and final for the impedance analyser to understand the possible charge transfer mechanism of the PANI-MnO_2@CF electrode.

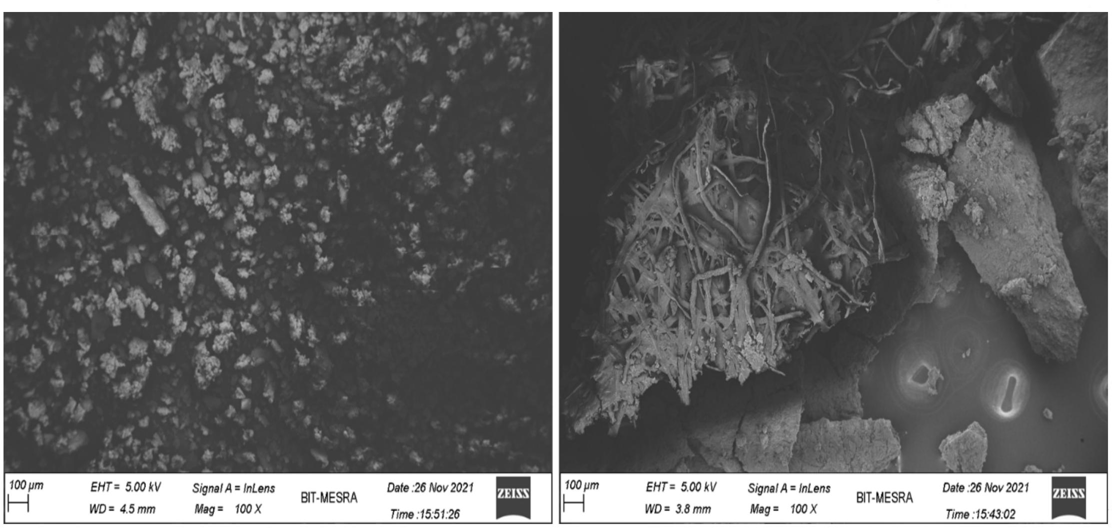
Result and discussion:

The peak observed below 730 cm^{-1} in the FTIR spectra of the PANI-MnO_2@CF is ascribed for the Mn-O vibration[12]. The peak obtained at 1496 and 1593 cm^{-1} is due to the $\vartheta_{c=c}$ stretching vibration of the benzene and quinoid ring respectively[13].



The peak at 1238 cm^{-1} is ascribed for the O-H bending vibration in the cotton fibre[14]. Along with this there is significant shift FTIR peak corresponding to $N = Q = N$ of PANI, $C = O$ and β-glycosidic linkage of the cotton fabric to 1092 cm^{-1}, 1015 cm^{-1}, 863 cm^{-1} indicates that there is strong interaction between the among the PANI@CF in the composite materials[15]. All other peaks are corresponds to PANI as supported by previously reports[16].

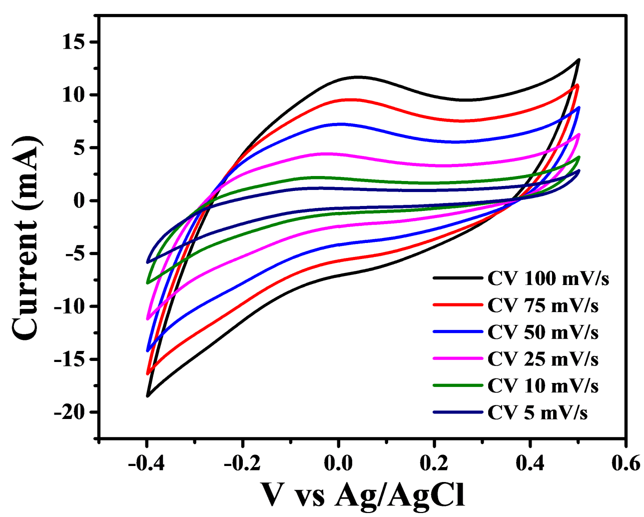
Surface morphology:



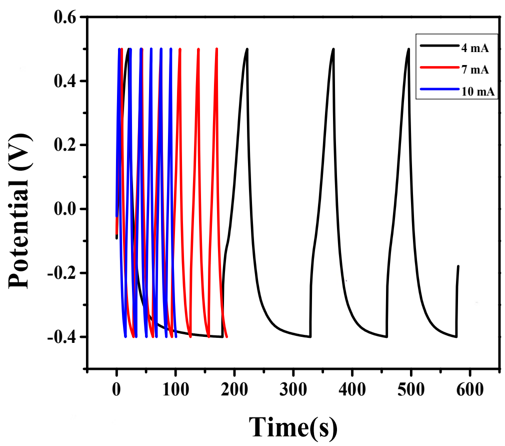
From the FESEM analysis it has been observed that the PANI has been successfully coated the over the surface of the MnO_2 and cotton fibre. Here, wrapping of cotton fibre over the PANI@MnO_2 surface can be observed exhibiting interconnected structure. Such morphology with uniform distribution of PANI@MnO_2 with cotton fibre allows the effective diffusion and penetration of electrolyte ions within material for good electrochemical performance.

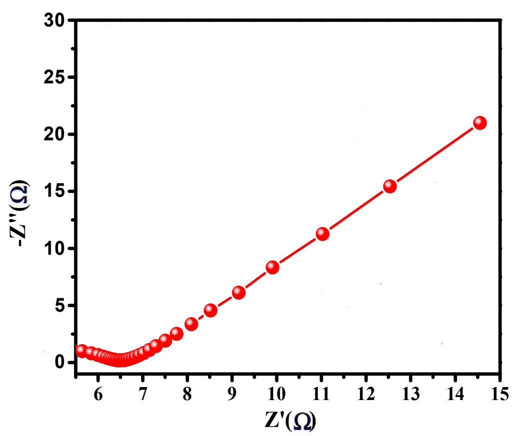
Electrochemical analysis of PANI-MnO_2@CF electrode material:

The CV of the as synthesised PANI-MnO_2@CF was performed at different scan rate from 5-100mVs using three electrode configurations where Ag/AgCl, Pt electrode is used as a reference electrode and 1M aq. KOH as an electrolytic solution. The CV analysis enable us to understand the redox behaviour of the electrode material. The potential window for the reaction is set to be at -0.4 to 0.5 V. Presence of spike in the voltammogram indicates that the electrode material undergoes redox reaction during the analysis process. This can be due to the reduction of the PANI during the electrochemical process[17]. The cotton fibre only acts as a backbone to enhance the flexibility of the electrode material.



With increases in the scan rate, it was observed that the cathodic peak slightly shifted towards the positive side. This is due to the resistance offered by the electrode material[17]. To validate the CV results GCD of the PANI-MnO_2@CF was performed. From charge-discharge plot, it is notable that profiles are non-linear in nature. This non-linearity could be ascribed to storage mechanism via electric double layer capacitance (EDLC) and pseudo-capacitance via PANI-MnO_2@CF. This clearly signifies the typical formation of hybrid electrode material. Similarly, frequency behaviour of synthesized material was also carried out by impedance spectroscopy in the form of Nyquist plot. Nyquist plot is the plot of real (Z') vs imaginary ($-Z''$) part. The X-intercept gives the solution resistance (Rs) whereas Y-intercept highlights the charge transfer resistance (Rct). As can be seen, Both Rs and Rctare observed to be very less which clarifies the lower resistance of synthesized material. This could be due to the formation of uniformly decorated PANI-MnO_2 over cotton fibre. Conducting nature of Polyaniline improves the semi-conducting behaviour of MnO_2 followed by stability provided by cotton fibre through its templating effect. This overall synergy imparted by all in a single interconnected conductive framework improves the electrochemical performance for supercapacitor application.





Conclusion :

MnO_2 decorated polyaniline (PANI) stabilized by cotton fibre was successfully synthesized by in-situ chemical oxidative polymerization. Bonding properties were confirmed by FTIR analysis whereas morphological analysis was performed by FESEM analysis. FESEM revealed the decoration of MnO_2-PANI on the cotton fibres. Electrochemical performances were also analysed by CV, charging-discharging and EIS analysis for the application in supercapacitor.

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