Synthesis and Electrochemical Analysis of Algae Cellulose-Polypyrrole-Graphene Nanocomposite for Supercapacitor Electrode

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A novel nanocomposite has been developed using extracted cellulose from marine algae coated with conductive polypyrrole and graphene nanoplatelets. The nanocomposite fabricated via in situ polymerization was used as an electrode for a supercapacitor device. The nanocomposite material has been electrochemically characterized using cyclic voltammetry to test its potential to supercapacitive behavior. The specific capacitance of polypyrrole-graphene-cellulose nanocomposite as calculated from cyclic voltammetry curve is 91.5 F g⁻¹ at the scan rate 50 mV s⁻¹. Transmission electron microscope images show the polymerized polypyrrole-graphene coated cellullosic nanofibers. Scanning electron microscope images reveal an interesting “necklace” like beaded morphology on the cellulose fibers. It is observed that the necklace like structure start to disintegrate with the increase in graphene concentration. The open circuit voltage of the device with polypyrrole-graphene-cellulose electrode was found to be around 225 mV and that of the polypyrrole-cellulose device is only 53 mV without graphene. The results suggest marked improvement in the performance of the nanocomposite supercapacitor device upon graphene inclusion.

Keywords: Supercapacitor, C. aegagropila, Cyclic Voltammetry, Graphene, Nanocomposite.

Depletion of non renewable fossil fuels and increased global warming due to rapid greenhouse gas emissions has forced us to move towards more efficient energy productions and use of renewable sources.¹,² Renewable sources of energies such as wind and solar power although being abundant are not available on demand. This has prompted the use of energy storage systems (ESS) like batteries, fuel cells and supercapacitors to store the surplus energy whenever available.³,⁴ Supercapacitors have gained much attention because of their higher power density as well as high energy density capabilities and fast charging which is suitable for various applications ranging from portable electronics, transportation vehicle, load leveling and many more.⁵ Supercapacitors also known as ultracapacitors store energy using either ion adsorption on highly porous electrode surface, electrochemical double layer capacitor (EDLC) or by fast surface redox reaction mechanism (pseudocapacitors).⁶ Pseudocapacitors tends to give higher energy density, higher capacitance as compared to EDLC however the phase changes within the electrode offset their structural stability, lifetime and power density.⁶ Therefore in order to achieve a supercapacitor electrode having higher performance as well as better stability, we consider a nanocomposite based on electrically conductive polymers and carbon based material. Electrically conducting polymers (ECPs) behave like pseudocapacitors such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTh).⁷⁹ Among them PPy has been of great focus because of its high specific capacitance, good thermal and chemical stability and environmentally friendly properties.¹⁰ Carbon based supercapacitors like graphene, reduced graphene oxide, carbon nanotubes and activated carbons have shown a superior performance primarily due to their very high specific surface area (SSA).⁵,¹¹–¹⁵ Nanocomposite based on PPy-graphene has been studied...
by various researchers in different electrode configuration and the method by which it has been synthesized. Previous attempts have been made to fabricate the electrode entirely from non metal. One of the ideal candidates is to use cellulose layer as substrate deposited using PPy. It has been shown that the paper based energy storage devices can be made using cellulose and a PPy composite. Cladophora algae cellulose is particularly of interest due to its abundant availability, ease of cellulose extraction, and significant mechanical strength as well as flexibility. The objective of this research is extraction of cellulose from C. aegagropila algae and fabrication of cellulose-PPy-graphene electrode using in situ polymerization followed by detailed electrochemical characterization of the nanocomposite for supercapacitor application.

Graphene nanoplatelets were purchased from Cheap-tubes Inc and they were used without further treatment. Pyrrole (Py) monomer and Iron Chloride (FeCl₃) was purchased from Sigma Aldrich. Electrochemical characterization was carried out using eDaq integrated potentiostat with aqueous electrolyte (1 M NaCl) with the three electrode setup where Pt was used as counter electrode (CE) and reference electrode (RE) was Ag/AgCl.

The cellulose was extracted from C. aegagropila algae using a modified protocol. 50 g of C. aegagropila algae was bleached using 18 g of NaClO₂ in acetic buffer to wash away impurities. The mixture was diluted to 50 ml and stored in a water bath for 2 hours. 300 ml of 0.10 M NaOH was added to the beaker, which was stored overnight. The pulp was neutralized with de-ionized water, and then dried, ground, and hydrolyzed by heating with H₂SO₄ in order to depolymerize the fibers. The pulp was allowed to stand overnight, and then washed to neutrality with de-ionized water to end the hydrolysis process.

Graphene nanoplatelets with varying concentration (1 mg and 3 mg) were dispersed in 10 ml Py solution in presence of 1 μl of polysorbate (Tween-80) surfactant for better dispersibility and adsorption on the cellulose. The solution was sonicated for 1 hr. The cellulose pulp was mixed with Py solution and then collected on filter paper. 8 g of FeCl₃ was dissolved in 100 ml of distilled water and run through the pulp to induce the polymerization for 10 min. A sponge like cake was formed at the end of polymerization process. The final product after polymerization was dried and it was given a rectangular shape with approximate thickness of 100 μm as shown in Figure 1 (Inset). Two samples were prepared (1) cellulose coated with PPy (PPy-cellulose) and (2) cellulose coated with PPy-graphene (PPy-graphene-cellulose). TEM images show individual cellulose fibers coated with PPy and graphene. Average diameter of cellulose fiber is 400 nm as shown in Figure 1(B) SEM image Figures 1(C), (D) shows an interesting beaded morphology of tween 80 surfactant self assembled in a “necklace” like structure. Beaded morphology starts to break upon increasing the concentration of graphene in the overall matrix. Polysorbate-80 was used as a surfactant to enhance the adsorption of pyrrole to the cellulose fibers. Since only a small quantity is required for effective adsorption of pyrrole to the surface of cellulose, the remaining amount might have been utilized by nonpolar graphene flakes, which attract to the hydrophobic tails of the polysorbate-80.

Figure 1. Transmission electron microscope images of (A) PPy-cellulose, (B) PPy-graphene-cellulose nanocomposite, Scanning electron microscope images (C) PPy-cellulose showing “necklace” like beaded morphology, (D) PPy-graphene of nanocomposite where long chains of beads starts to break. (Inset (A), (B) Optical images of nanocomposite made of cellulose extracted from marine algae, (A) PPy-cellulose, (B) PPy-graphene-cellulose.
molecules. As a result, graphene is buried within the substrate, which contains polar, hydrophilic regions that the other end of the polysorbate-80 molecules can attach to. The device was assembled as shown in Figure 2 with two electrodes placed on either side of whatmann’s filter paper as a separator soaked with the 1 M NaCl electrolyte placed in between.

The electrochemical response of the PPy-cellulose and PPy-graphene-cellulose electrodes was determined from cyclic voltammetry measurement. The working electrodes (WE), PPy-cellulose or PPy-graphene-cellulose with thickness of 100 μm and 0.64 cm² area were used to perform electrochemical studies. Figures 3(a), (b) shows the voltammogram plots at 50 mV s⁻¹ scan rate of both nanocomposite electrodes. The PPy-cellulose electrode weighs about 7.2 mg and PPy-graphene-cellulose weight was 6 mg. The specific capacitance of the electrodes have been determined using following equation.

\[ C = \frac{1}{2mV} \int_{V^-}^{V^+} I(V) dV \]  

Where \( C \) is the specific capacitance (F g⁻¹), \( m \) is the mass of electrode (g), \( V = V^+ - V^- \) the potential difference and \( s \) is the scan rate (mV s⁻¹). The specific capacitance of the PPy-cellulose electrode was 73.32 F g⁻¹ at the scan rate of 50 mV s⁻¹ and PPy-graphene-cellulose electrode has 91.5 F g⁻¹. The variation in the specific capacitance of PPy-cellulose and PPy-graphene-cellulose nanocomposite as a function of scan rate is shown in Figure 4. At the scan rate of 10 mV s⁻¹ the specific capacitance of PPy-cellulose nanocomposite is 572 F g⁻¹ and that of PPy-graphene-cellulose is 630 F g⁻¹. At 50 mV s⁻¹ the specific capacitance of PPy-cellulose nanocomposite is 73.32 F g⁻¹ whereas PPy-graphene-cellulose gives 91.5 F g⁻¹. The specific capacitance of the nanocomposite goes higher at low
Figure 4. Variation of specific capacitance of PPy-cellulose and PPy-graphene-cellulose nanocomposite as a function of scan rate. (Inset: Specific capacitance change as function of graphene concentration at scan rate of 50 mV s$^{-1}$).

scan rates because the $\alpha$-C atoms of the PPy ring have been almost oxidized to form C$-$C bonds in the process of polymerization. So some $\alpha$-C at the end of polymer chain and $\beta$-C atoms of the PPy chains could be oxidized/deoxidized. When the scan rate is low, these atoms are not only oxidized/deoxidized, but also the doping ions have enough time to inject/eject from the PPy particles freely.$^{24}$ Figure 4 (inset) shows the specific capacitance of the nanocomposite with varying graphene concentration. At a scan rate of 50 mV s$^{-1}$ nanocomposite without graphene (0g) has specific capacitance of 73.32 F g$^{-1}$, nanocomposite with 1mg graphene has 76.49 F g$^{-1}$ and with 3 mg of graphene the specific capacitance was 91.5 F g$^{-1}$. An increasing specific capacitance trend is observed with the increase in graphene concentration in the nanocomposite.

Multimeter was used to measure electrical potential of the nanocomposite devices. The self-discharge rate of the devices was investigated by measuring the open circuit voltages for several days. Figures 3(C), (D) illustrates the full potential of the PPy-graphene-cellulose device was approximately 3.5 times that of the PPy-cellulose device. It is apparent that device containing PPy-cellulose electrodes started to discharge after about two days, whereas the device containing PPy-graphene-cellulose electrode began discharging after about three days.

1. CONCLUSION

This work demonstrates the use of the sustainable and abundantly available cellulose extracted from $c.$ aegagropila algae coated with polypyrrole and graphene as an electrode for supercapacitor application. The nanocomposite was fabricated using in situ polymerization of Py monomer mixed with graphene. The introduction of high specific surface area graphene nanoplatelets enables the nanocomposite to achieve high specific capacitance of 91.5 F g$^{-1}$. The nanocomposite exhibits better electrochemical performance with graphene. SEM and TEM clearly show the deposition of PPy on the cellulose fibers. SEM reveals beaded structure which is formed by the polysorbate which is a surfactant used to disperse graphene in polypyrrole solution. The beaded structure breaks upon increasing the concentration of graphene in the nanocomposite.

Author Contributions

Ashish Aphale, Aheli Chattopadyay, Kapil Mahakalkar carried out the experiments. Prabir. K. Patra, Aheli Chattopadyay and Ashish Aphale conceptualized and designed the experiments. Prabir. K. Patra advised the whole team. All authors contributed during the manuscript preparation. All authors have given approval to the final version of the manuscript.

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References and Notes

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