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Surfactant assisted polyaniline nanofibres—Reduced graphene oxide (SPG) composite as electrode material for supercapacitors with high rate performance

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ABSTRACT

We have synthesized a composite of surfactant assisted polyaniline nanofibres and graphene oxide (SPGO) followed by reduction to prepare surfactant assisted polyaniline nanofibres-reduced graphene oxide (SPG) composite. The performance of the synthesized composite has been compared with the SPGO, PANI and reduced graphene oxide (rGO). The prepared samples have been characterized by Field effect scanning electron microscopy (FESEM), X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) techniques. The electrodes prepared from these samples have been tested for their electrochemical performances using cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedence spectroscopy (EIS), in a two electrode configuration. The CV results revealed that the SPG cell has higher voltammetric current as compared to SPGO, PANI and rGO cells leading to better capacitive nature. From charge discharge studies, the SPG cell exhibits maximum specific capacitance of 444 Fg^{-1} at 0.6 A g^{-1} with good retention after 2000 charge discharge cycles. The specific energy and power density of the SPG cell is observed to be 13.36 W h kg^{-1} and 1.03 kW kg^{-1}, respectively, which is significantly large as compared to SPGO, PANI and rGO cells. The EIS studies showed enhanced rate performance of SPG cell as compared to the rGO and PANI cell which is in agreement with the CV results. These results make it a promising candidate for supercapacitor applications.

1. Introduction

Energy storage devices are those devices which store and release energy when required. Some common examples include batteries, capacitors, fuel cells, supercapacitors etc [1]. Supercapacitors, also called ultracapacitors, have emerged as powerful sources of energy over the last few years, because of their capacity to deliver much larger capacitance values than the other capacitors [2,3] and higher power density [4]. Supercapacitors, on the basis of their mechanisms, can be classified into two categories, namely, electric double layer capacitances (EDLCs) and pseudocapacitances [5,6]. Supercapacitors based on EDLCs usually employ carbon based materials such as activated carbon [7], mesoporous carbon [8], nanoporous carbon [9,10], and carbon nanotubes [11] as electrode materials. These EDLCs store energy electrostatically via electrical double layer of charge formed by the charges in the electrode itself and ions in the electrolyte [12]. Since there is no transfer of charges, these EDLCs have long cycling stability but shows lower capacitance values due to non contribution of some micropores of these electrode surfaces [13]. The size of these micropores is very small preventing large electrolyte ions to diffuse into the electrode surface [14]. On the other hand, the pseudocapacitors achieve high capacitances through the Faradaic reactions such as oxidation reduction reactions between the electrode and the electrolyte [2]. Supercapacitors based on pseudocapacitors utilize conducting polymers such as polyaniline (PANI) [15], polypyrrole (PPY) [16] and polythiophenes (PTH) [17] etc. and metal oxides such as manganese dioxide [18], ruthenium oxide [19] as electrode materials. PANI is considered as one of the most promising conducting polymers applicable as electrodes in the supercapacitors, due to its simple cost effective synthesis process [20], tunable electrical conductivity [21] and its reversible redox behavior. Polyaniline exists in four different forms i.e. leucomeraldine base, emeraldine base, emeraldine salt, and pernigraniline form which are inter-convertible into one another depending upon the oxidation reduction and doping de-doping processes [22]. However, the Faradaic redox processes occurring between the electrode and the electrolyte affect its stability during

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charging discharging processes [23]. We have tried to exploit both Faradaic as well as non-Faradaic behavior by synthesizing a composite of PANI with reduced graphene oxide, so as to achieve the maximum capacitance and cycling stability. We have also attempted to compare the behavior of the composite with either of the PANI and bare rGO in terms of capacitance, cycling stability and rate performance of the cells.

Graphene is a two dimensional monolayer of carbon atoms arranged in a hexagonal lattice, discovered in 2004 by Geim and Novoselov [24]. It has many unusual electrical, thermal, and mechanical properties due to high carrier mobility at room temperature [24], high thermal conductivity [25], and superior young modulus [26] respectively. Moreover, it is considered as an appropriate material for substrates, as it has large surface area [5] estimated theoretically and can be combined with other nanomaterials making it suitable for many applications such as supercapacitors, batteries, transparent conducting electrodes, solar cells, and gas sensors [27–31] etc. It is difficult to prepare single layer graphene for many such applications, so at times, many layer reduced graphene oxide (rGO) becomes more suitable.

For rGO based polymer composites, it is important to grow nanomaterials uniformly on the reduced graphene oxide sheets to improve its overall capacitive properties. Therefore, we report the synthesis of surfactant assisted polyaniline nanofibres reduced graphene oxide (SPG) composite by in-situ polymerization of aniline in the presence of graphene oxide (GO) dispersion and cationic surfactant CTAB. The GO sheets in the composite were then reduced to reduced graphene oxide by using hydrazine hydrate via hydrothermal method, followed by reoxidation and reprotonation in presence of HCl and APS for changing the state of PANI from leucomeraldine to the emeraldine form.

2. EXPERIMENTAL

2.1. Preparation of GO, rGO, PANI, SPGO and SPG composite

2.1.1. Graphene oxide (GO)

Graphene oxide was synthesized via Improved Hummer's method [32,33]. Graphite flakes (3.0 g, Sigma Aldrich) and potassium permanganate (18 g) were kept in a round bottom flask in a low temperature bath at 0 °C. A mixture of conc. H_2SO_4/H_3PO_4 (360:40 ml) was poured into it. The reaction mixture was heated to 50 °C along with continuous magnetic stirring for 12 h. After cooling the reaction mixture to 27 °C, it was then mixed with ice (~400 ml). Complete oxidation of graphite flakes was indicated by the appearance of a bright yellow color on adding 30% H_2O_2 (3 ml). The mixture was then centrifuged for 10 min at 6000 rpm, followed by washing with de-ionized water, hydrochloric acid, ethanol, and ether, repetitively. The solid obtained was then dried at 60 °C in a vacuum oven to give a grey colored powder.

2.1.2. Reduced Graphene oxide (rGO)

For reduction, 100 mg GO was dispersed in 100 ml water in a round bottom flask and kept in an ultrasonicator for 1 h to ensure the homogeneity of GO dispersion. After this, 1 ml hydrazine hydrate was added to the solution and heated under a water cooled condenser at 100 °C for 24 h. Upon heating, the solid material precipitated out as black powder which was then collected by centrifugation, followed by washing with de-ionized water and methanol. The black colored solid obtained was then dried overnight in vacuum oven at 80 °C.

2.1.3. Polyaniline Graphene oxide (SPGO) and polyaniline reduced graphene oxide composites (SPG)

1 gm of GO was added to the de-ionized water, followed by ultrasonication for 1 h to obtain a homogeneous GO dispersion. Thereafter, 30 mM of CTAB was added to it and stirred for 30 min. 1 M of hydrochloric acid (HCl) and 0.1 M of doubly distilled aniline were added to the solution and stirred for further 30 min to ensure the uniformity of the dispersion. Then, the 0.1 M Ammonium persulphate (APS) was added to 100 ml de-ionized water, followed by ultrasonication for 30 min. The two solutions were mixed rapidly at 0 °C under continuous stirring. The reaction was performed for 6 h at 0 °C under constant stirring. The reaction mixture was left for 12 h for stabilization and completion of polymerization. The reaction was completed by adding methanol, followed by centrifugation for 10 min. The solid product obtained after centrifugation was washed with de-ionized water and methanol, and dried at 60 °C for 24 h in a vacuum oven to give a green color powder. For comparison, surfactant assisted PANI nanofibres were synthesized in the same manner but with no graphene oxide added to the solution.

For the synthesis of SPG composites, the SPGO composite was re-dispersed in a solution of 0.1 M APS solution and 1 M HCl was added to the solution and stirred overnight. The SPG composite was collected by centrifugation, followed by washing with de-ionized water and methanol, and drying overnight at 60 °C to have a green colored powder of SPG composite.

2.2. Characterization methods

The surface morphology of prepared samples were analyzed using Field effect scanning electron microscopy (FESEM) images (Model: FE-SEM, Tescan, MIRA3) in secondary emission mode and Transmission electron microscopy (TEM) images using HRTEM FEI, Technai G^2T30, U-Twin. The synthesis of the composites were confirmed by Fourier transform infrared spectroscopy (FTIR) spectra in the wavenumber range of 400–4000 cm^{-1} on FTIR spectrum RX1 Perkin-Elmer spectrometer, UK and X-ray diffraction (XRD) data, recorded at D8 Discover (ASX-Bruker) X-ray diffractometer using Cu-K_α radiation. The Raman spectral measurements were performed on all the samples using Renishaw InVia Reflex micro Raman spectrometer where air cooled argon laser of wavelength ~514.5 nm is used as a source.

2.3. Preparation of electrodes and electrochemical measurements

The prepared samples were tested for their electrochemical performance using the supercapacitor cells in a two electrode configuration. To prepare the electrodes, a mixture was prepared by grinding samples, acetylene black and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as binder in the ratio of 70:10:20 (w/w) respectively. After grinding for about half an hour, slurry was prepared by mixing acetone in the above mixture. The prepared slurry was then coated on flexible graphite sheets, followed by drying overnight at 100 °C. The area of the prepared electrodes was 1 cm^2. The mass of the prepared SPG, PANI, SPGO, and rGO electrodes was measured by weighing the graphite electrodes before and after coating. Symmetric cells were prepared by stacking two identical electrodes over one another separated by the filter paper, soaked with the electrolyte (1 M H_2SO_4).

The electrochemical characterizations of the prepared cells were performed using cyclic voltammetry (CV), galvanostatic charge discharge (GCD) tests and electrochemical impedence spectroscopy (EIS) techniques. The CV and EIS performances of the prepared cells were evaluated with an electrochemical analyzer 660E, CH Instruments, USA. The frequency range for EIS measurements varies from 10 m Hz to 100 kHz with ac voltage amplitude of 10 mV. In CV, the applied potential varies from −0.2 V to 0.8 V. The charge-discharge measurements were carried out at constant current density using a charge-discharge unit, BT-2000, Arbin