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Polypyrrole-Decorated Hierarchical $NiCo_2O_4$ Nanoneedles/Carbon Fiber Papers for Flexible High-Performance Supercapacitor Applications

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ABSTRACT

A novel polyprrole (PPy)-decorated hierarchical $NiCo_2O_4$ nanoneedles was grown on highly conductive carbon fiber paper (CFP) for high performance asymmetric supercapacitor applications. The PPy-decorated hierarchical $NiCo_2O_4$ nanoneedle on CFP (PPy-$NiCo_2O_4$@CPF) was grown by two steps. At first, $NiCo_2O_4$ nanoneedle was grown by hydrothermal process and followed by the deposition of PPy through electrochemical method. The fabricated PPy-$NiCo_2O_4$@CPF electrode displayed the higher electrochemical performance. The specific capacitance was ~910 F g-1 at a current density of 1 A g^{-1} and cyclic stability was ~88% after 10,000 cycles. To explore real performance of the electrode, we have fabricated solid state asymmetric supercapacitor using PPy-$NiCo_2O_4$@CFP as positive and nitrogen doped reduced graphene oxide (N-rGO) as negative electrodes. The fabricated asymmetric device delivered a specific capacitance of 118.6 F g-1 at a current density of 1.0 A g^{-1} with a maximum energy density of 40.81 Wh Kg^{-1} (at a power density of 738.27 W Kg^{-1}) and maximum power density of 3746.77 W Kg^{-1} (at an energy density of 13.53 Wh Kg^{-1}). The impressive results suggest that flexible PPy-$NiCo_2O_4$@CFPs can be a promising electrode material for supercapacitor applications.

1. Introduction

Electrochemical capacitors (ECs) have the advantages of higher specific power, fast charge-discharge capabilities and long cycle life when compared to batteries [1,2], and highly desirable for applications in different domains such as power sources for portable electronics, electric/hybrid vehicles, and a number of microdevices [3–5]. ECs use two distinctly different charge mechanisms to develop capacitance: electric double-layer capacitance through an electrostatic charge development between the electrode/electrolyte interfaces, and pseudocapacitance developed from highly reversible Faradaic reactions process occurring at specific potentials [6–9]. The resulting capacitors are called electric double-layer capacitors (EDLC) and pseudo-capacitors.

Recent advances in nanomaterials and new designs have yielded a distinct improvement in the performance, which has enabled the achievement of a higher energy density together with a significant power density to support extensive utilization for ECs in future applications [10]. The endeavors to address the problem of lower capacitance and energy density in research and industry alike have been focused on the development of electrode and electrolyte materials [11]. From early applications of porous activated carbon (AC), carbon continues to demonstrate suitability as an electrode in a variety of distinct material designs [12]. However, main problem remains in enhancing the energy density when these materials are used independently, which is due to their manner of energy storage and lower specific surface area. Meosporous and hierarchical template carbon materials have demonstrated their capabilities for their applications by possessing high energy and correspondingly high-power density [13]. To data, pseudocapacitive materials such as metal oxides [14,15], conducting polymers [16,17] have been used substantially to improve the performance of the ECs. Among them, transition metal

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oxides have been extensively attracted as promising electrode materials for supercapacitors, due to their higher specific capacitances than other materials [18].

A growing interest has been paid on the development of supercapacitor electrode using conductive substrates as a binder-free electrode, which have many advantages like higher conductivity, accessible electroactive sites and easy to flow electrolyte to the electrode surface. Here we introduce highly conductive and flexible carbon fiber paper (CFP) support for the decoration of electroactive material as a working electrode as well as a current collector. Among transition metal oxides, $NiCo_2O_4$ has been intensively used as a promising electrode material for the pseudocapacitors due to its higher charge storage capacity and relatively low cost as compared to other metal oxides [19–23]. Further, it possessed much better electrical conductivity and higher redox activity compared to single NiO and Co_3O_4 [24,25]. In our previous work, we reported that the core/shell-like $NiCo_2O_4$ decorated-multiwall carbon nanotube (MWCNT) electrodes showed a miximum specific capacitance of 822 F g^{-1} at a scan rate of 5.0 mV s^{-1} [26]. In this work, we have fabricated polypyrrole (PPy)-decorated hierarchical $NiCo_2O_4$ nanoneedle on CFP (PPy-$NiCo_2O_4$@CPF) via a hydrothermal synthesis and electrochemical deposition method, and its supercapacitive properties were evaluated as a binder free electrode for flexible supercapacitor application.

2. Materials and Methods

2.1. Materials

Nickel(II) nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$, 99.0% assay, (Sigma-Aldrich), cobalt (II) nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$, 99.0% assay and pyrrole (Sigma-Aldrich) were utilized as precursors without further modification. Poly(acrylonitrile) (PAN) based chopped CFs (fiber length: 6 mm) were purchased from Toho Tenax Co. Ltd, Japan, and used to fabricate CFP without further purification. Phenol resin (Phenolite KC-6301) was purchased from Kangnam Chemical Co. Ltd., Republic of Korea. Polyvinyl alcohol (PVA, Mw 89,000–98,000 g mol^{-1}) was purchased from Sigma-Aldrich. All the reagents were of analytical grade and used without further purification. All the aqueous solutions were prepared with deionized water (18.2 Ω M-cm, Elga DI water system).

2.2. Fabrication of carbon fiber paper (CFP)

For the dimensional stability of CFPs, physical bonding between each carbon fiber (CF) presented in the paper was induced by mixing with aqueous phenol as a binder, according to previous paper making method [27]. In order to prepare uniformly dispersed CFs slurry, CFs (1.4 g) were added into 10 wt% phenol aqueous solution (1000 ml) and then stirred using a mechanical stirrer for 10 min. The resultant slurry was filtered and dehydrated on 200 mesh screen. The circular shaped CFPs with basic weight of 70 g m^{-2} and diameter of 160 mm were obtained. After dehydration, the obtained CFPs were dried at 80 °C for 60 min, and then further pressed using a hot-pressing machine with a load of 500 kg at 130 °C for 5 min. Afterwards, the CFPs were carbonized using a horizontal tubular furnace (Pyrotech Co., Ltd., Republic of Korea) at the temperature for 30 min under N_2 atmosphere, by heating up to 900 °C with heating rate of 10 °C min^{-1} [28].

2.3. Fabrication of polypyrrole (PPy)-decorated hierarchical $NiCo_2O_4$ nanoneedle on CFP (PPy-$NiCo_2O_4$@CPF)

The polypyrrole (PPy)-decorated hierarchical $NiCo_2O_4$ nanoneedle on CFP (PPy-$NiCo_2O_4$@CPF) was prepared by two-step process. At first, $NiCo_2O_4$ was prepared by a hydrothermal method. The detailed experimental procedures are as follows. The hydrothermal solution was prepared by dissolving the Ni $(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and urea in 70 ml ethanol solution. The prepared pink color solution was transferred to Teflon container and then carbon fiber paper (CFP) was immersed into the solution. The hydrothermal process was carried out at 120 °C for 12 h, and after reaction the reactor was cooled down to room temperature naturally. The obtained $NiCo_2O_4$ coated CFP was removed from hydrothermal reactor and washed with ethanl and water for multiple times to remove the unreacted precursors as well as loosely deposited $NiCo_2O_4$ from surface of carbon fiber paper. Secondly, polypyrrole (PPy) was coated on the $NiCo_2O_4$ modified CFP by using electrochemical deposition method. For polypyrrole deposition, a three electrode configuration was used in which $NiCo_2O_4$ coated CFP acts as a working electrode, Ag/AgCl as a refrence and Pt wire as counter electrode. The deposition precess was carried out at a scan rate of 50 mV s^{-1} with potential of −0.2–1.0 V for 15 cycles in the electrolyte solution containing 0.5 M KCl and 100 μl of pyrrole monomer.

2.4. Synthesis of N-doped reduced graphene oxide (N-rGO)

The nitrogen doped reduced graphene oxide (N-rGO) was prepared by two step process. Firstly, graphene oxide (GO) was prepared by modified Hummer's method and detailed preparation was described in our previous report [29]. The prepared 0.2 g of GO was dispersed in 100 ml ethanol under sonication for 2 h. And then, 2 ml of cyanamide solution as a N-dopant was added to the GO solution under stirring at 80 °C and stirring was further continued overnight at 80 °C. Then the final product was dried at 120 °C for 3 h in vacuum furnace and annealed at 900 °C for 3 h under N_2 at a heating rate of 5 °C min^{-1} [30].

2.5. Fabrication of all solid state asymmetric supercapacitor

All solid state asymmetric supercapacitor device was fabricated using PPy-$NiCo_2O_4$@CFP as a positive and N-rGO as a negative electrode with PVA-KOH gel electrolyte. We have prepared PVA-KOH gel electrolyte according to previous report [31]. The prepared both positive and negative electrodes were dipped for 5 min in PVA-KOH gel to allow electrolyte to fill the electrodes and allowed to dry at room temperature for few hours. Finally, semi- dried positive and negative electrodes were assembled by sandwiching the filter paper (Chmlab group, 125 mm Ø, Spain) as a separator between two electrodes. Briefly, the asymmetric supercapacitor was fabricated asymmetric PPy-$NiCo_2O_4$//N-rGO device using PPy-$NiCo_2O_4$@CFP as a positive electrode and N-rGO as a negative electrode with the size of 1 cm × 3 cm separated by filter paper. Prior to assemble the device, both electrodes and filter paper was soaked into 1.0 M KOH electrolyte for 5 min. The working area of the final device was around 1 cm × 1 cm.The assembled device was dried at room temperature for several hours to remove the excess water from the gel and finally, the prepared device was bagged with polyethelene paper. The 1.0 M KOH solution was used as a liquid electrolyte for all electrochemical measurements.