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Tricobalt tetroxide nanoplate arrays on flexible conductive fabric substrate: Facile synthesis and application for electrochemical supercapacitors

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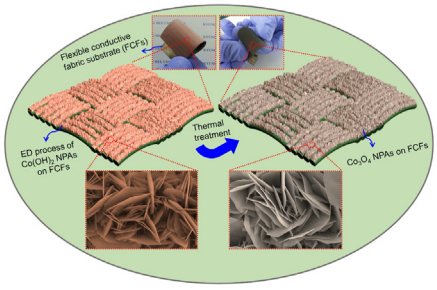
HIGHLIGHTS

- Co_3O_4 nanoplate arrays (NPAs) were fabricated on flexible conductive fabric substrate (FCFs).
- The Co_3O_4 NPAs were uniformly entrapped on FCFs with good adhesion.
- Optimized growth of Co_3O_4 NPAs on FCFs leads to a superior electrochemical performance in supercacpitors.

GRAPHICAL ABSTRACT



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ABSTRACT

Tricobalt tetroxide (Co_3O_4) nanoplate arrays (NPAs) were synthesized on flexible conductive fabric substrate (FCFs) by a facile two-electrode system based electrochemical deposition method, followed by a simple heat treatment process. Initially, cobalt hydroxide ($Co(OH)_2$) NPAs were electrochemically deposited on FCFs by applying an external voltage of −1.5 V for 30 min. Then, the Co_3O_4 NPAs on FCFs was obtained by thermal treatment of as-deposited $Co(OH)_2$ NPAs on FCFs at 200 °C for 2 h. From the analysis of morphological and crystal properties, the Co_3O_4 NPAs were well integrated and uniformly covered over the entire surface of substrate with good crystallinity in the cubic phase. Additionally, the fabricated sample was directly used as a binder-free electrode to examine the feasibility for electrochemical supercapacitors using cyclic voltammetry and galvanic charge−discharge measurements in 1 M KOH electrolyte solution. The Co_3O_4 NPAs coated FCFs electrode exhibited a maximum specific capacitance of 145.6 F/g at a current density of 1 A/g and an excellent rate capability after 1000 cycles at a current density of 3 A/g. This facile fabrication method for integrating the Co_3O_4 nanostructures on FCFs could be a promising approach for advanced flexible electronic and energy-storage device applications.

1. Introduction

In recent years, there has been an urgent demand in the development of flexible, wearable and light-weight devices for electronic and energy storage applications [1–3]. Among various energy storage device, supercapacitors (SCs) or ultra-capacitors

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have attracted considerable attention owing to their promising characteristics of ultra-high power delivery, rapid charge–discharge capability, long cycle life, high efficiency, low cost, and safe operation [4–6]. These properties are highly desirable in various applications including electronic devices, backup energy systems, and hybrid electric vehicles [7–10]. In general, SCs are classified into two different types depending upon their charge storage mechanism: one is electrical double layer capacitors (EDLCs) (carbon nanotubes, graphene, activated carbon materials) and the other is psuedocapacitors (metal/metal oxides and their composites nanomaterials), which offers much higher capacitance than the EDLCs [11–13]. To date, innovative progress has been made for developing the electroactive materials and current collectors for superior electrochemical properties in SCs applications [14–17]. To enhance the electrochemical properties, free-standing and binder-free electrode with a rational nanostructure design under optimal growth condition would be essential [18–20]. Accordingly, extensive research efforts have been devoted to the fabrication of metal/metal oxide electroactive materials on various conductive substrates, i.e., a popular fabrication method for SCs [21,22]. In particular, there have been many reports on synthesizing the Cobalt (Co) based compounds and composite nanostructures on various conductive substrates for SCs. For example, Wang et al. reported the growth of vertically aligned $CoMoO_4$ nanoplate arrays on Nickel (Ni) foam electrode for SCs [23], Wu et al. prepared the nanowall arrays of Co_3O_4 on Ni foam substrate [24], Duan et al. synthesized the Co_3O_4 nanoflakes on Ni foil, Zhang et al. obtained the free-standing mesoporous $NiCo_2O_4$ nanosheets on Ni foam, Ti foil and stainless steel substrates [21], and Woo et al. reported the growth of Zn–Co LDH nanosheets on ITO glass from an aqueous metal salt solution with hydrogen peroxide as an oxidant [25]. Unfortunately, the above mentioned nanostructures have been mainly achieved in a time-consuming hydrothermal growth process and in most cases, these kinds of nanomaterials have been synthesized on expensive, low-flexibility and rigid substrates by complicated fabrication methods, which limits their usage in energy storage devices. Meanwhile, the carbon textile based substrates have been utilized as a flexible electrode to decrease the rigidity of substrates for further extending the energy storage devices applications. Chao et al. prepared the hierarchical Co_3O_4 nanosheet arrays on carbon textile [26], and Chen et al. synthesized the Nickel cobalt sulfide nanosheet arrays on carbon cloth for flexible asymmetric SCs using a three electrode system based electrochemical deposition method [17]. Nevertheless, the carbon cloth which is also expensive substrate cannot be wearable as garments and a reference electrode would be needed for this growth process [27]. Despite their great progress, however, there have been little works on the direct growth of electroactive materials on cost-effective fabric based substrates for SCs using facile growth methods [28]. As compared to other expensive electrodes, commercially available flexible conductive fabric is considered as a new kind of substrate for SCs because of its advantageous properties like cost-effective production, possibility to use in clothing, high conductivity and flexibility [27,29]. Notably, these substrates are weaved by intertwined fibers in the fabric framework, which provides a high surface area for efficient electron transportation and facilitates the diffusion of electrolyte into the electroactive materials. These attractive properties of conductive fabrics are favorable for wearable electronic and energy storage device applications [30].

Among various transition metal oxides, tricobalt tetroxide (Co_3O_4) is an excellent electroactive material in SCs because of its novel physical and electrochemical properties [31,32]. Moreover, due to the low cost, ease of availability, and efficient charge storage property, Co_3O_4 nanostructures can be effectively utilized in lithium-ion batteries, gas sensors, catalysis, and electronic devices [33–36]. Generally, the Co_3O_4 exhibits different types of nanostructures such as nanowires, nanoplates, nanorods, nanocubes, nanoflowers, etc. by various growth methods [4,37–40]. In SCs, electrochemical properties of these nanostructured materials depend on their size, morphology, and ability to adhere on the surface of current collectors [41,42]. Particularly, the Co_3O_4 nanostructures with nanoplate morphology can be expected to an excellent electroactive material for SCs due to their strong adhesion to the substrate, large surface area, and efficient electrolyte ions penetration [43]. To synthesize these Co_3O_4 nanostructures, an electrochemical deposition (ED) method has been utilized as a facile and rapid fabrication method for the growth of variety of nanostructures on conductive substrates [43,44]. By applying an electric field in growth solution, various nanostructures were simply fabricated on SCs electrodes [45]. Moreover, this method offers binder-free electrodes for SCs with short growth time, low-cost (for low reaction temperature, low deposition voltages) and uniform deposition of nanostructures on conductive substrates [46].

In this work, we demonstrated a facile and cost-effective growth of Co_3O_4 nanoplate arrays (NPAs) on flexible conductive fabric substrate (FCFs) using the two electrode system based electrochemical deposition (ED) method without any reference electrode, followed by simple heat treatment process. By controlling the applied external voltage, the NPAs were uniformly decorated on FCFs with good adhesion. The effect of applied external voltage on the morphology of NPAs was investigated. Also, the electrochemical properties of the Co_3O_4 samples were analyzed by cyclic voltammetry (CV), galvanic charge–discharge (GCD) characteristics and electrochemical impedance spectroscopy (EIS) measurements.

2. Experimental details

2.1. Chemicals

All the chemicals were of analytically pure grade and were used without any further purification. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were purchased from Sigma–Aldrich Corporation (South Korea). Potassium hydroxide (KOH) was obtained from DaeJung Chemicals (South Korea).

2.2. Preparation of Co_3O_4 NPAs on FCFs

The Co_3O_4 NPAs were grown on FCFs via a simple ED, followed by thermal treatment. Prior to the ED process, commercially available nickel (Ni) coated polyethylenterephthalate (PET) fibers woven conductive fabric substrate was chosen and it was cut into pieces with a size of ~2×2.5 cm^2. Then, the pieces were cleaned by rinsing with acetone, ethanol, and de-ionized (DI) water, respectively. Meanwhile, the growth solution was prepared by mixing the equimolar concentrations of both $Co(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}N_4$ (i.e., 10 mM) with 800 ml of DI water (resistivity of 18 MΩ-cm) at room temperature. As a result, the growth solution exhibited a pink color in the ED beaker. After the growth solution was heated at 75–80 °C on hotplate, the FCFs was carefully immersed into the growth solution with the counter electrode by keeping the distance of 1 cm. Herein, a simple two-electrode system was utilized with a working electrode (i.e., FCFs) and a platinum (Pt) mesh as the counter electrode [29]. During the ED process, the growth temperature was maintained to 75–80 °C and different external voltages were applied from −0.5 to −3.0 V for optimized growth condition. After 30 min, the sample was carefully removed from the experimental setup, rinsed with DI water and dried by flowing nitrogen gas at room temperature. Then, the cobalt hydroxide ($Co(OH)_2$) NPAs