



Intense pulsed white light assisted fabrication of Co-CoOx core-shell nanoflakes on graphite felt for flexible hybrid supercapacitors



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ARTICLE INFO

Article history:

Received 31 January 2017

Received in revised form 15 June 2017

Available online 17 June 2017

Keywords:

Intense pulsed white light
hybrid supercapacitor
nanostructure
energy storage
cobalt oxide

ABSTRACT

In this work, cobalt/cobalt oxide (Co-CoOx) core-shell nanoflakes were directly grown on flexible graphite felt (GF) using a facile one-step intense pulsed white light (IPWL) irradiation method. They were then used as a battery-type positive electrode for a high-performance asymmetric hybrid supercapacitor, which exhibited high rate capability and a long cycle life. The interconnected Co-CoOx thin nanoflakes grown on the GF offer large reaction sites and enough space for easy OH⁻ ion transport due to their 3-dimensionally interconnected network structures. Cobalt metal at the core of the nanoflakes, directly connected to the current collector of the GF, provided pathways for electrons between the cobalt oxide and GF, leading to low internal resistance and high rate capability. The Co-CoOx/GF electrode had a high specific capacity of 108 mAh g⁻¹ at a specific current of 1 A g⁻¹ and maintained a capacity of 71 mAh g⁻¹ at a high specific current of 20 A g⁻¹. A two-terminal asymmetric hybrid supercapacitor, assembled using Co-CoOx/GF as the positive electrode and activated carbon as the negative electrode with gel-electrolyte (PVA/KOH), exhibited an energy density of 30.1 Wh kg⁻¹ at a power density of 0.86 kW kg⁻¹ and a high retention of 13.0 Wh kg⁻¹ at a power density of 20.4 kW kg⁻¹. In addition, the asymmetric device showed excellent cycling stability, with 114% capacity retention after 10,000 cycles.

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1. Introduction

Because interest in flexible electronics is increasing, many researchers in recent years have made efforts to develop flexible and bendable energy storage devices [1–5]. In general, energy storage devices consist of three key components: a current collector, an active material, and a separator/electrolyte [1]. For flexible energy storage devices, these components should be able to perform appropriately under mechanical bending strain. Among the components, the current collector significantly influences the performance of flexible devices because it occupies a substantial part of the device and because the mechanical strength and electrical properties of the flexible device mostly depend on the mechanical and electrical properties of the current collector [6]. Therefore, in designing flexible and bendable energy storage systems, selection of suitable current collectors and supporting

substrates is important. Recently, graphite felt (GF) [7], carbon cloth [8,9], and carbon textiles [10,11] have been investigated as current collectors for flexible electrodes. Among them, GF is an excellent supporting substrate/current collector due to its reasonable electrical conductivity, high electrochemical stability, and high porosity and mechanical flexibility [7,12].

Supercapacitors have greater cycle stability and faster charge-discharge time than Li-ion batteries, but their energy density is poorer [13–15]. The energy density of a supercapacitor is determined by the specific capacitance and operating voltage, indicating two possible approaches for improvement: expanding the operating cell voltage and increasing the capacitance [16–18]. Electrical double-layer capacitors (EDLCs) that are based on carbon materials can achieve higher capacitance in aqueous electrolytes than in organic electrolytes, but they operate in a limited potential range (<1 V) in aqueous electrolytes due to water decomposition [14,18–22]. One efficient way to improve the energy of an aqueous electrolyte-based supercapacitor is to design a hybrid system composed of a faradaic non-capacitive battery-type positive electrode and a non-faradaic capacitive EDLC-type negative electrode. The energy density of the hybrid system can then be

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enhanced because the battery-type materials, such as metal hydroxides ($\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$) [23,24] and metal oxides (NiCo_2O_4 , NiO , Co_3O_4 , CoO) [25–28], have a high theoretical capacity based on faradaic redox reactions via transitions between multiple oxidation states. However, metal hydroxide- and oxide-based energy storage devices have limited power density because of their low electronic conductivity [29–31]. This phenomenon becomes more conspicuous when these materials are applied to carbon-based flexible substrates such as GF, carbon cloth, and carbon textiles because of their lower electrical conductivity compared with conventional metal current collectors such as Ni foams, stainless steel, and Al foil. One efficient way to improve the rate capability of battery-type positive electrodes is to design hierarchical structures for the electrode materials for easy charge diffusion and transfer [32–35]. Another way to improve the rate capability of the electrode is to increase the electrical conductivity of the electrode materials by designing metal/metal oxide (or hydroxide) core-shell-type hetero-structures. With a core-shell structure, the electrically conductive metal core can facilitate the transport of electrons between the current collector and the shell of the metal oxide (or hydroxide), which can result in enhanced rate capability and power for metal hydroxide- and oxide-based energy storage devices. In addition, because the conductivity of electrode materials greatly influences the electrochemical properties, highly conductive materials show low polarization, which results in high utilization of the active materials and enhanced electrochemical performance. Therefore, growing metal/metal oxide core-shell electrodes directly on carbon-based flexible substrates can create high-performance flexible and bendable energy storage devices.

Another issue in metal hydroxide- and oxide-based energy storage devices is the synthesis of nanostructured metal oxides/hydroxides. 3D-nanostructured metal hydroxides/oxides have been synthesized using various methods, including hydrothermal [26–28,36], microwave [37,38], chemical precipitation [39], and solution methods [40]. Typically, those methods require high annealing temperatures and long reaction times to convert metal-precursors into metal oxides. In addition, when metal oxides need to be incorporated with conductive materials, the method involves multiple steps. Therefore, facile, fast, energy-efficient methods for metal oxide/hydroxide 3D-nanostructure production are of interest.

In this study, we report an extremely facile approach to fabricating binder-free 3D-nanostructured cobalt oxide (CoOx) incorporated with conductive Co metal (Co) on a flexible current collector using a simple one-step intense pulsed white light (IPWL) technique. IPWL irradiation transfers heat energy in the form of light from a xenon lamp that emits a light spectrum in the visible region [41]. Cobalt metal/cobalt oxide (Co-CoOx) core-shell nanoflakes are fabricated on GF by irradiating $\text{Co}(\text{NO}_3)_2$ -coated GF substrate with IPWL for a few milliseconds under atmospheric pressure at room temperature. The Co-CoOx core-shell nanoflakes on GF exhibit high rate capability and excellent cycling stability. The interconnected Co-CoOx nanoflakes offer many electroactive sites for faradaic reactions with electrolyte and porous spaces for easy ion/charge diffusion. In addition, the incorporated cobalt metal, which connects the active CoOx to the current collector in the GF, facilitates electron transfer between the CoOx and GF and minimizes the internal resistance of the electrode, resulting in high electrochemical performance. In addition, Co contributes to the structural stability of the electrode during cycles.

2. Experimental

2.1. Preparation of Co-CoOx nanoflakes on GF by IPWL irradiation

Prior to IPWL irradiation, the GF substrate was electrochemically oxidized by applying a constant potential of 2 V for 90 s in an aqueous solution of 0.5 M H_2SO_4 using a CHI 660D electrochemical workstation (CH Instrument) to improve the wettability of the GF to the metal oxide precursor solution. The GF substrate was washed with acetone and deionized (DI) water several times and dried at 60 °C for 6 hr. After that, the GF substrate was soaked in 0.4 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution for 10 min. After drying in a vacuum at 50 °C for 2 h, the metal oxide precursor-coated GF was irradiated under IPWL at a total energy of 30 J cm^{-2} with two pulses (10 ms on time and 30 ms off time) at room temperature in ambient conditions. The distance between the sample and xenon lamp was a few millimeters. After irradiation, the samples were washed with DI water several times to remove residue and dried in an oven at 60 °C. The mass loading of CoOx-Co was about 0.8 mg and the thickness of the as-prepared electrode including GF was 0.9 mm. The mass of GF ($1 \times 2 \text{ cm}^2$) was 14 mg.

2.2. Preparation of activated carbon (AC) electrodes

The negative electrodes for the asymmetric hybrid supercapacitor were prepared by mixing AC (MSC-30, Kansai Coke & Chemicals Co. Ltd.), poly(vinylidene fluoride) (M.W. 534,000, Sigma-Aldrich), and carbon black (Super P, TIMCAL Graphite & Carbon) in a weight ratio of 8:1:1. A small amount of N-methyl-2-pyrrolidone (Sigma-Aldrich) was added to form a slurry. A doctor blade was used to cast the carbon slurry on graphite foil. Then, the coated electrodes were dried at 90 °C for 3 h to remove all solvents.

2.3. Integration of asymmetric hybrid supercapacitors

An asymmetric hybrid supercapacitor was constructed by sandwiching the Co-CoOx/GF (positive electrode) and the AC (negative electrode) with a PVA/KOH gel-electrolyte. The gel-electrolyte was fabricated by mixing 8 g of poly(vinyl alcohol) (PVA, M.W. 89,000–98,000) and 4 g KOH in 60 mL of DI water under vigorous stirring at 80 °C for 1 h. The gel-electrolyte was spread over the electrodes using a glass rod. Then, the gel-electrolyte-coated electrodes were put under vacuum for 5 min at 40 °C to remove air bubbles. After that, the gel electrolyte-coated electrodes were solidified for 6 h at room temperature. The size of each electrode was $1 \times 2 \text{ cm}^2$ and the total thickness of an asymmetric hybrid supercapacitor was 1.15 mm.

2.4. Material characterization

The structure and morphology of the fabricated samples were studied using field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) and field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL). To analyze the crystal structures, X-ray diffraction (XRD, D8 Advance, Bruker) measurements were examined with monochromatized $\text{Cu-K}\alpha$ radiation. The volume fractions of the crystals appearing in the samples were estimated by calculating the area of a main peak of each crystal which was fitted by using a Gaussian function. The pore structure and Brunauer-Emmett-Teller (BET) surface area were measured using an Autosorb-iQ 2ST/MP (Quantachrome) analyzer at 77.35 K.

2.5. Electrical conductivity measurement

The electrical conductivity of the GF and Co-CoOx/GF was measured using a four-probe conductivity measurement system

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