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Synthesis of Co_3O_4 nanosheets via electrodeposition followed by ozone treatment and their application to high-performance supercapacitors

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HIGHLIGHTS

- Thin film of $Co(OH)_2$ nanosheets is converted to Co_3O_4 by UV–ozone treatment.
- Synthesis of Co_3O_4 film is done at low temperature on flexible substrate.
- The specific capacitance of the film after UV–ozone treatment reaches 1033.3 F g^{-1}.
- The capacitance is more than 10 times higher than the film before the treatment.
- Still 77% of specific capacitance remains after 3000 cycles of charge/discharge.

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ABSTRACT

A thin film of Co_3O_4 nanosheets is electrodeposited on a flexible Ti substrate by a one-step potentiostatic method, followed by an UV–ozone treatment for 30 min. The films before and after the UV–ozone treatment are characterized with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The film is composed of $Co(OH)_2$ before UV–ozone treatment, and of Co_3O_4 after the treatment. The morphologies of both films are examined by scanning electron microscopy (SEM) and transmission electron microscope (TEM). The obtained films are composed of nanosheets, and there is no change in their sheet-like morphology before and after the UV–ozone treatment. When applied for a supercapacitor, the Co_3O_4 modified Ti electrode (Co_3O_4/Ti) shows a far higher capacitance than that of the $Co(OH)_2$ modified Ti electrode. The electrodeposition time and NaOH concentration in the electrolyte are optimized. A remarkably high specific capacitance of 1033.3 F g^{-1} is obtained for the Co_3O_4 thin film at a charge–discharge current density of 2.5 A g^{-1}. The long-term stability data shows that there is still 77% of specific capacitance remaining after 3000 repeated charge–discharge cycles. The high specific capacitance and long-term stability suggest the potential use of Co_3O_4/Ti for making a flexible supercapacitor.

1. Introduction

Energy storage is one of the major challenges in recent years due to the fast-growing demand for high-performance energy storage devices for consumer electronics, electric vehicles, and medical electronics [1]. Among several kinds of energy storage devices, electrochemical capacitors (supercapacitors) became eye-catching, because of their high power density, high energy efficiency, and long charge–discharge cycle life [2]. Supercapacitors can be classified into two categories, electrochemical double-layer capacitors (EDLCs) and electrochemical pseudocapacitors (EPCs), depending on their energy storage mechanism. An electrochemical double-layer capacitor (EDLC) is usually based on the capacitance of one of its electrodes (with or without a film) arising due to the charge separation at this electrode/electrolyte interface. An electrochemical pseudocapacitor (EPCs) is usually based on the capacitance of one of its electrodes arising from fast and reversible faradic redox reactions within the electroactive material on this electrode. Much attention has been paid on the EPCs, in recent years, due to their superior energy density than that of EDLCs [3]. Several metal oxides, e.g., RuO_2 [4], MnO_2 [5], and NiO [6] have been investigated as the electrode materials for pseudocapacitors. Among these, Co_3O_4 has attracted considerable interest in the field of pseudocapacitors, due to its excellent redox activity and environmental friendliness [2]. The theoretical specific capacitance of Co_3O_4 is 3560 F g^{-1} [2]. Besides, the nano-scale morphology of Co_3O_4 thin film is known to affect its redox activity in a significant way [7].

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In order to obtain a high specific capacitance for a Co_3O_4 thin film in a pseudocapacitor, various Co_3O_4 nanostructures, e.g., nanotubes [3], nanowires [2], nanoparticles [8], and nanosheets [1] have been investigated. Recently, Qing et al. synthesized a film of Co_3O_4 nanoflowers on a Ni foam substrate by solvothermal method, and achieved a remarkably high specific capacitance of 1936.7 F g^{-1} [9] for its capacitor. In most of the works on Co_3O_4 based EPCs, calcination or annealing process was used to prepare Co_3O_4 thin films, which is energy-consuming and unsuitable in the case of several kinds of flexible substrates. Lightweight and flexible capacitors have advantages of easy transportation and roll-to-roll production, which makes them cost-effective. It is important to develop a simple and low-temperature process to prepare thin films of Co_3O_4 on flexible substrates.

UV–ozone treatment has been applied for several decades for surface cleaning of substrates or thin films [10]. The short-wavelength UV light can efficiently decompose O_2 in the air to produce ozone, and both the UV light and the produced ozone gas play important roles in the removal of the contaminant molecules on the surface of substrates or films [11]. Besides, due to strong oxidative ability of O_3 towards organics, the convenient vapor treatment is used for the removal of organic layers on the surfaces of nanostructures [12]. In addition to the applications for surface cleaning and removing of organics, the UV–ozone treatment is utilized to functionalize carbon nanotubes and carbon black; this way of functionalization is convenient and milder, with reference to the conventional way of functionalization by oxidative treatment, using acidic vapors or strong oxidants [13,14].

In this study, a thin film of cobalt oxide nanosheets was synthesized on a flexible Ti foil, first by a one-step, fast electrodeposition of a film, and then by an UV–ozone treatment to the electrodeposited film. An excellent specific capacitance of 1033.3 F g^{-1} was observed for the thin film of Co_3O_4, at a charge–discharge current density of 2.5 A g^{-1}. To the best of our knowledge, this is the first time to use UV–ozone treatment to convert a cobalt hydroxide thin film to Co_3O_4; the obtained Co_3O_4 thin film shows an excellent specific capacitance. The UV–ozone treatment is fast and simple for the conversion of cobalt hydroxide thin film to Co_3O_4 thin film at a relatively low temperature, and is a promising technique for the low-temperature preparation of nanostructural metal-oxide thin films on flexible substrates.

2. Experimental

2.1. Chemicals

Cobalt nitrate 6-hydrate (A.C.S. reagent, J.T. Baker), ammonium fluoride (A.C.S. reagent, J.T. Baker), nitric acid (65%, Sigma–Aldrich), isopropyl alcohol (99%, Sigma–Aldrich), and sodium hydroxide (A.C.S. reagent, J.T. Baker) were used as received. Deionized water (DIW) was used throughout the work.

2.2. Apparatus

Potentiostatic electrodeposition, cyclic voltammetry (CV), and chronopotentiometric experiments were performed with a CHI 440 electrochemical workstation (CH Instruments, Inc., USA). A conventional three-electrode system was used in all the electrochemical experiments, mentioned above. A polished and cleaned Ti foil was used as the working electrode for the electrodeposition, and the Ti foil modified with the cobalt hydroxide or cobalt oxide was used as the working electrode for the CV and chronopotentiometric experiments. For all experiments, a Pt foil (4.0 cm × 1.0 cm) and an Ag/AgCl/saturated KCl (homemade) were used as the counter and reference electrode, respectively. All electrochemical experiments were performed at room temperature and all the potentials were reported against the Ag/AgCl/sat'd KCl reference electrode.

Nanostructures of the cobalt oxide films were observed by using scanning electron microscope (SEM, Nova NanoSEM 230) and transmission electron microscope (TEM, Hitachi H-7100, Japan). The selected area electron diffraction (SAED) patterns were also obtained by the same TEM apparatus. The structural characterizations of the films of cobalt hydroxide and oxide were verified by X-ray diffraction patterns (XRD, X-Pert, the Netherlands) with Cu K_α radiation. The powder of cobalt oxide scraped from its' film was also characterized by the same XRD apparatus. The compositions of the films of cobalt hydroxide and oxide were verified by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe system, ULVAC-PHI, Chigasaki, Japan), using a microfocused (100 μm, 25 W) Al X-ray beam, with a photoelectron takeoff angle of 45°. The Ar^+ ion source (FIG-5CE) was controlled by using a floating voltage of 0.2 kV. The Wienfiltered C_{60}^+ ion source (IOG C60-10, Ionoptika, Chandler's Ford, UK) was operated at 10 mA and 10 kV. The binding energies obtained in the XPS analyses were corrected for specimen charging, by referencing the C 1 s peak to 284.60 eV. UV–ozone cleaning machine (Jelight Company, Inc., Model No. 42) was used for the UV–ozone treatment for the thin films, throughout the work.

2.3. Preparation of the flexible Co_3O_4 modified Ti electrode

A flexible Ti foil (0.1 mm, 99.5%) was polished and cleaned first by the following procedure. First, the Ti foil was soaked in a 65% nitric acid solution containing 0.2 M of ammonium fluoride for 15 min, in order to etch the oxidized and contaminated layers on the surface, and was washed by DIW. Thereafter, the Ti foil was soaked and sonicated first in isopropyl alcohol, and then in DIW. The sonicated period for each step was 5 min. After finishing this polishing and cleaning procedure, the Ti foil was used for the deposition of a thin film of Co_3O_4. The thin film was synthesized by a one-step potentiostatic electrodeposition, followed by an UV–ozone treatment. The electrodeposition process was carried out potentiostatically at −1.0 V with respect to an Ag/AgCl/KCl (sat'd) reference electrode. The polished and cleaned flexible Ti foil was used as the working electrode with an exposed area of 0.5 cm^2, and a Pt foil was used as the counter electrode. A solution of 0.10 M cobalt nitrate 6-hydrate was used as the electrolyte for the electrodeposition process. The electrodeposition time was chosen as 4 min. Thereafter, the electrode modified with the electrodeposited film was subjected to the UV–ozone cleaning for 30 min in air. A flexible Ti electrode modified with Co_3O_4 was thus obtained. For comparison, another type of Ti electrode modified with Co_3O_4 was also obtained by annealing the electrodeposited film at 200 °C for 1 h.

2.4. Estimation of mass of the thin films

In order to calculate the specific capacitance of the thin films, the mass of the films were estimated by Faraday's law, on the assumption that Faraday's current efficiency for electrodeposition was 100%. The reactions for the cathodic electrodeposition process in the solution containing nitrate ions have been reported in several literatures and can be expressed as follows [15–18],

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$2OH^- + Co^{2+} \rightarrow Co(OH)_2 \quad (2)$$

According to these reactions, the total number of cobalt ions in the electrodeposited film could be calculated from the total charge