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Ethanol-assisted solvothermal synthesis of porous nanostructured cobalt oxides (CoO/Co_3O_4) for high-performance supercapacitors

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HIGHLIGHTS

- The CoO/Co_3O_4 is synthesized by one-step solvothermal method without calcination.
- The CoO/Co_3O_4 nanocomposites possess a high specific surface area.
- CoO/Co_3O_4 nanocomposites exhibit good capacitance and excellent cycle life.
- The CoO/Co_3O_4 electrode shows lower R_s.

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ABSTRACT

The porous mixed-phase CoO/Co_3O_4 nanocomposites have been prepared by a facile ethanol-assisted solvothermal approach without a subsequent calcination process and the composites are formed by aggregations of many nanoparticles with an average diameter of 5 ± 2 nm. The porous structures are verified by BET test results with a typical type-IV isotherm curve and a high surface area (~186.27 $m^2\,g^{-1}$). Electrochemical properties are characterized by cyclic voltammetry, galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy. The CoO/Co_3O_4 electrode exhibits a high capacitance of 451 Fg^{-1} at a current density of 1 Ag^{-1}, which is higher than that of the pure CoO electrode (203 Fg^{-1}). Interestingly, the CoO/Co_3O_4 shows a low equivalent series resistance (0.16 Ω) and superior cycle stability (108% retention after 5000 cycles). Moreover, an asymmetric supercapacitor based on this hybrid CoO/Co_3O_4 and activated carbon can deliver an energy density of 10.52 Wh kg^{-1} at a power density of 140 W kg^{-1}. These results indicate the CoO/Co_3O_4 composites will be a promising electrode material for high-performance supercapacitor applications.

1. Introduction

Electrochemical capacitors (supercapacitors), with irreplaceable properties of long service lifetime, fast charge–discharge process, green environmental protection and high energy efficiency, have been widely employed in the power back-up systems, public transportation and medical devices, etc., [1,2]. Supercapacitors (SCs) are generally of two varieties based on the charge storage mechanism: electric double-layer capacitors (EDLCs) and faradaic pseudocapacitors. The former can store charge electrostatically using charge accumulation on electrode materials' surface due to the electrostatic force rather than Faradaic reaction, leading to high power density and long cycle lifetime [3]. The latter, however, use the fast and reversible redox reaction at the surface of active materials, which exhibit higher capacitance and superior energy density than EDLCs. Electrode material as the main factor to determine the performance of the SCs has received more and more attention. To date, carbon materials, metal oxides/hydroxides, conducting polymers, metal sulfides and their compounds have been identified as most promising materials for SCs [4].

Among the different types of metal oxides, Co_xO_y [5,6], NiO [7], MnO_2 [8], RuO_2 [9], have been widely investigated due to variable oxidation states of metal ions which facilitate redox transitions and higher charge storage. Cobalt oxides receive more intense attention owing to their high theoretical specific capacitance, low

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cost, good corrosion stability and environmentally friendly nature [10], especially have been applied in pseudocapacitors as electrode material and prove to be a potential alternate to expensive RuO_2. Up to now, various processing techniques have been adopted to tailor the structures of Co_3O_4 and thereby enhance its electrochemical properties. For example, Wang et al. reported fabrication of Co_3O_4@MWCNT nanocable using a simple hydrothermal procedure and it presented excellent rate capability for SCs [11]. Kumar et al. prepared Co_3O_4 nanofibers by electrospinning technique with a specific capacitance of 407 Fg^{-1} at a scan rate of 5 $mV\,s^{-1}$ [12]. Luo et al. synthesized three-dimensional (3D) enoki mushroom-like Co_3O_4 hierarchitectures by a reflux method and it exhibited a high specific capacitance of 787 Fg^{-1} at a current density of 1 Ag^{-1} [13]. Unfortunately, after the above-mentioned hydrothermal, electrospinning or reflux technique is applied, usually, a subsequent calcination process is necessary for preparing perfect Co_3O_4, which adds much uncertainty about morphology control and reproducibility [14,15].

In addition, cobalt monoxide (CoO), another kind of cobalt oxide, is also highly electrochemically active, as unveiled in SCs application. Nevertheless, less attention has been paid to CoO, which is hard to synthesize because of the special requirements necessary to force cobalt in a low oxidation state under common ambient conditions and unavoided introductions of impurities [16]. According to the theoretical capacitances, the theoretical capacitance of pure CoO and Co_3O_4 are 4292 and 3560 Fg^{-1} [17], respectively, which indicates CoO can also be a good candidate for pseudocapacitor electrode material. However, both CoO and Co_3O_4 suffer from the problems of poor electrical/ionic conductivity during the charging–discharging process and limited surface area, resulting in the poor cycling performance [3]. Therefore, it is still a great challenge to make a balance between excellent pseudocapacitive performance and simplicity of the synthetic pathway [18].

In order to better use cobalt oxides in supercapacitors, in this work, we apply a one-step solvothermal approach to prepare mixed-phase CoO/Co_3O_4 nanocomposites with relatively high specific surface area in high yield. The CoO/Co_3O_4 nanocomposites possess a strong synergistic effect because of the common redox reactions related to Co–O/Co–O–OH, which provide a good capacitive retention and stability under corrosive alkaline conditions [19]. Its discharge capacitance as a electrode material for supercapacitors is 451 Fg^{-1} at the current density of 1 Ag^{-1}. Interestingly, the CoO/Co_3O_4 nanocomposites show a slight increase for specific capacitance after 5000 cycling tests. Furthermore, an asymmetric supercapacitor is fabricated using the CoO/Co_3O_4 electrode and activated carbon as the positive and negative electrodes, respectively, which exhibits an energy density of 10.52 Wh kg^{-1}.

2. Experiment

2.1. Synthesis of CoO/Co_3O_4 nanocomposites and CoO spheres

All the chemicals were of analytical grade without further purification. The typical synthetic experiments were as follows: Solution A: 0.800 g of cobalt acetate ($Co(Ac)_2$) was dissolved in a 40 mL of absolute ethyl alcohol system under agitated stirring for 2 h. Solution B: 0.256 g of sodium hydroxide was dissolved in 40 mL of absolute ethyl alcohol to get a transparent solution. A dark turbid solution formed when solution B was added to solution A slowly and regularly. The mixed solution was stirred for 3 h before transferred into the stainless steel autoclaves with a Teflon liner of 100 mL in capacity, which was then heated in an oven at 160 °C for 8 h. After cooled to room temperature naturally, the products were obtained by centrifugation and washed with absolute ethanol for several times (CAUTION: the products could only be washed with absolute ethanol and water addition resulted in the appearance of homogeneous mixture), and finally dried in air at 80 °C. The preparation of CoO spheres was the same as the CoO/Co_3O_4 nanoparticles except that 0.4369 g of ammonia (25 wt%) was added instead of 0.256 g of sodium hydroxide. The production efficiencies of CoO spheres and CoO/Co_3O_4 nanoparticles are >90%.

2.2. Material characterization

The scanning electron microscopic (SEM) images of the materials were obtained by a field-emission scanning electron microscope (SU8020, HITACHI). Transmission electron microscopy (TEM) micrographs were obtained from an FEI Tecnai G2 S-twin transmission electron microscope with a field emission gun operating at 200 kV. Chemical compositions and crystallite structures of the samples were determined by XRD (Rigaku D/max-2550, Japan) using Cu Kα radiation from 10 to 80 angles. Nitrogen (N_2) adsorption–desorption isotherm measurements were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer at 77 K. Before adsorption–desorption isotherm measurements, the samples were outgassed at 80 °C for 10 h in the degas port of the analyzer. The X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MK II electron spectrometer.

2.3. Electrochemical measurements

The supercapacitor electrodes were prepared by mixing an as-prepared active material, acetylene black and polytetrafluoroethylene emulsion (PTFE) with a weight ratio of 8:1:1. A small amount of deionized water was added to improve the mixing. Then the resultant slurry was homogeneously pasted onto porous Ni foam, which was pressed under a pressure of 10 Mpa and dried at 75 °C for 24 h. The loading mass of active material was $\sim$2.0 mg·cm^{-2}.

For the three-electrode mode measurements, the as-prepared CoO or CoO/Co_3O_4 single electrode was directly used as working electrode, a platinum electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrochemical performance was evaluated by cyclic voltammetry, galvanostatic charge–discharge technique and electrochemical impedance spectroscopy using an electrochemical workstation (IVIUMSTAT; Ivium Technologies, Netherlands). All the tests were made at room temperature in a 3 M KOH aqueous solution. According to the three-electrode data, the specific capacitance (SC) of the single electrode material was calculated from the CVs and discharge curves with the Eqs. (1) and (2), respectively [12].

$$C_s = \int i(u)du/m\upsilon\Delta V \tag{1}$$

$$C_s = I\Delta t/m\Delta V \tag{2}$$

where C_s (Fg^{-1}) is the specific capacitance, m (g) represents the mass of the active material, υ ($mV\,s^{-1}$) is the potential scan rate, $i(u)$ (A) is the voltammetric current, ΔV (V) is the potential drop during discharge, I (A) is charge–discharge current,) Δt (s) is the discharge time.

Moreover, asymmetric capacitor was fabricated by assembling the CoO/Co_3O_4 nanoparticles and the activated carbon (AC) as anode and cathode separated by a porous non-woven cloth in a CR2032-type coin cell. The optimal mass ratio of $m(CoO/Co_3O_4)/m(AC)$ should be about 1.32 in the asymmetric supercapacitor, which is based on charge balance theory and their respective specific capacitances [20,21]. The specific capacitance is calculated by the two-electrode data following Eq. (2), except that