Journal of Power Sources 217 (2012) 358–363

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Mesoporous Co_3O_4 materials obtained from cobalt–citrate complex and their high capacitance behavior

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HIGHLIGHTS

- The mesoporous Co_3O_4 materials are synthesized from cobalt-citrate complex.
- The mesoporous Co_3O_4 materials have a large surface area of 129 $m^2\ g^{-1}$.
- The forming mechanism of mesoporous Co_3O_4 materials has been proposed.
- Mesoporous Co_3O_4 materials exhibit excellent electrochemical performance.

ARTICLE INFO

Article history:
Received 20 October 2011
Received in revised form
10 March 2012
Accepted 29 May 2012
Available online 13 June 2012

Keywords:
Electrochemical capacitors
Cobalt oxide
Cobalt–citrate complex
Cobalt hydroxide
Mesoporous

ABSTRACT

In this work, amorphous and mesoporous Co_3O_4 material is obtained from the calcination of loosely packed $Co_3O_4/Co(OH)_2$ nanosheets which are synthesized by the formation and disassociation of cobalt–citrate complex reaction. We propose that Co nanoparticles are completely oxidized to form the stable cobalt–citrate complex in the presence of sodium citrate and oxygen, and cobalt–citrate complex disassociates to $Co(OH)_2$ under alkaline conditions. The high surface area and mesoporous texture of granular Co_3O_4 materials are the consequence of the energetically favored topotactic transformation aspect in the solid-state oxidative reaction. Furthermore, mesoporous Co_3O_4 material exhibits excellent electrochemical capacitance prosperities, well retention to the discharging capacity in cycle lifetime, and a high specific capacitance of 427 F g^{-1}, indicating its potential application in electrochemical capacitors and further in energy and environmental applications.

1. Introduction

Cobalt oxide (Co_3O_4) represents an important class of inexpensive and environmentally benign materials with the potential applications in catalysts [1], magnetics [2], and high-performance electrochemical devices [3,4]. To design high-performance electrode materials in term of electrochemical activity, kinetic feature, retention to the discharging capacity in cycle lifetime, and understanding charge storage mechanism affect electrochemical performance is of great importance [5,6]. Recent studies prove that pseudocapacitors based on Co_3O_4 materials show much enhanced capacitance and greatly improved energy density compared with electric double-layer capacitors (EDLCs) [7–9]. However, there are still significant drawbacks of these Co_3O_4 pseudocapacitors, namely, the limited cyclical stability and poor rate capability of the Co_3O_4 electrode, which remain major challenges for use in practical batteries. These problems have long been partly attributed to low conductivity of metal oxides and phase transition (structural rearrangements) under the fast and reversible redox reaction at the surface of the electro-active materials in the charging/discharging electrochemical process [10–12]. The key to achieving high specific capacitance Co_3O_4 pseudocapacitors with long cycle life is to prepare nano-structured or micrometer-scale Co_3O_4 electrode materials with rational design of material morphology, size, and structure, which are critical to the electrochemical reactivity and lifetime based on reducing both the ionic and electronic path within the particles. Torsten Brezesinski et al. [10] proposed that mesostructured and nano-structured architectures for transition metal oxides facile both redox and intercalation pseudocapacitance

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http://dx.doi.org/10.1016/j.jpowsour.2012.05.115

from alleviating the need of long-range diffusion of ions through the van der Waals gaps as well as amorphous structure can provide surface sites for redox pseudocapacitance. Recent advances in material preparation technologies enable electrode materials to be readily prepared with tunable particle size, shape and structure. For example, Zhu et al. [13] had synthesized Co_3O_4 materials with three different structures (one-dimensional needle-like nanorods, two-dimensional leaf-like nanosheets, and three-dimensional oval-shaped microparticles) by controlling the concentration of polyethylene glycol and water solution, which exhibit the promising capacitive properties. Mesoporous Co_3O_4 monolayer hollow-sphere array was fabricated by electrodepositing from aqueous solution containing cobalt precursor and exhibits a specific capacitances of 358 F g^{-1} at 2 A g^{-1} [14]. With the exposed crystal plane (112), Co_3O_4 nanomesh obtained from pyrolysis of the precursor of $(NH_4)_2Co_8(CO_3)_6(OH)\cdot 4H_2O$ and showed the high capacitances (155–198 F g^{-1}) and good rate capability [15].

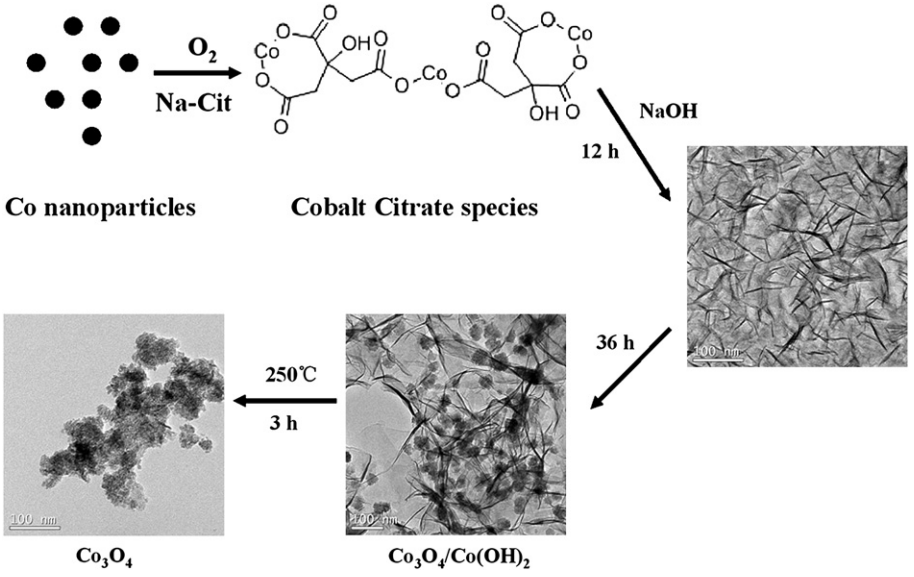
Beyond that, there is a novel strategy basing on the rational design of complex reaction to prepare metal oxides with tunable particle size, shape and structure. Earlier examples of this strategy for the formation of cobalt oxides, such as CoO nanorods from Co–Oleate complex [16], Co_3O_4 nanotubes from (cysteinato-N,S) bis(ethylenediamine)cobalt(III) complex [17], hollow Co_3O_4 nanowire arrays from $[Co(NH_3)_6]_2^+$ [18], and CoO/Co_3O_4 composite nanocrystal from unknown complex [19], have been elegantly reported. It is anticipated that cobalt complex can be obtained by taking control of the rate of complex reaction and will serve as the precursor to fabricate meso-structural Co_3O_4 with the enhanced electrochemical performance.

Herein, we firstly report the preparation of amorphous and mesoporous Co_3O_4 nanomaterial which obtains from the pyrolysis of loosely packed $Co_3O_4/Co(OH)_2$ nanosheets based on the reaction of the formation and disassociation of cobalt–citrate complex. We propose that Co nanoparticles are completely oxidized to form the stable cobalt–citrate complex in the presence of sodium citrate and oxygen, and cobalt–citrate complex is disassociated to $Co(OH)_2$ under alkaline conditions. The high surface area and mesoporous texture of granular Co_3O_4 material might be the consequence of the energetically favored topotactic transformation aspect in the solid-state oxidative reaction. Furthermore, mesoporous Co_3O_4 material exhibits excellent electrochemical capacitance prosperities, well retention to the discharging capacity in cycle lifetime, and a high specific capacitance of 427 F g^{-1} that is obtained at a charge/discharge current density of 1.25 A g^{-1}, suggesting its potential applications in electrochemical capacitors and further in energy and environmental applications, such as lithium batteries, CO catalysis, and electrochemical evolution of oxygen.

2. Experimental

All solvents and chemicals are of reagent quality and are used without further purification. $Co(NO_3)_2\cdot 6H_2O$, sodium citrate (Na-Cit), $NaBH_4$, NaOH, and sodium lauryl sulfate (SDS) are obtained from Shanghai Chemical Reagent Co. All aqueous solutions were freshly prepared with deionized water. Scheme 1 shows the synthesis route of the mesoporous Co_3O_4 materials. In typical synthesis, 60 mg $Co(NO_3)_2\cdot 6H_2O$ and 180 mg Na-Cit were firstly dissolved in 30 ml distilled water under magnetic stirring. To this mixture, 5 ml of ice-cold $NaBH_4$ (0.1 M) was rapidly injected with stirring vigorously, generating a black solution. The whole solution was kept stirring vigorously for 2 h at room temperature to promote the oxidation of Co nanoparticles completely to form the stable cobalt–citrate species, as suggested by the color change of the solution from black to violet (Fig. S1). Then, 3 mg SDS and 60 mg NaOH dissolved in 5 ml distilled water were added to the mixture immediately. The reaction mixture was stirring vigorously for 5 min, and then left undisturbed at 30 °C for 36 h. Finally, a typical teal blue solid was shown, indicating the formation of $Co_3O_4/Co(OH)_2$ hybrid. The teal blue solid was collected and washed several times with ethanol and distilled water by centrifugation at 10,000 rpm, and finally dried at 80 °C for 4 h. By a subsequent thermal treatment at 250 °C for 3 h in air, the tea-blue $Co_3O_4/Co(OH)_2$ materials were changed into black Co_3O_4 powder. The more details of mechanism of Cobalt–Citrate Complex reaction were showed in supplementary material.

Transmission electron microscope (TEM) was carried out by using a JEOL JEM-2100 (Japan) operated at 200 kV. Morphology of the synthesized products was examined using a JEOL JSM-6701F (Japan) field emission scanning electron microscope (SEM). Wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-2400 (Japan) with Cu Kα radiation (40 kV,



Scheme 1. Synthesis of meosporous Co_3O_4 materials from cobalt-citrate complex.