Materials Letters 65 (2011) 1986–1988

Contents lists available at ScienceDirect

Materials Letters

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

Hydrothermal synthesis of ultra fine β-$Co(OH)_2$ nanowires with novel morphologies using supercritical water

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ARTICLE INFO

Article history:
Received 1 December 2010
Accepted 27 December 2010
Available online 15 March 2011

Keywords:
Cobalt hydroxide
Nanowire
Forest
Pan trees
Single crystalline

ABSTRACT

Different morphologies of single-crystalline β-cobalt hydroxide (β-$Co(OH)_2$) nanostructures are successfully synthesized in large quantities by a facile hydrothermal synthetic method with cobalt powder as the cobalt source, supercritical water and triethylamine as both an alkaline and a complexing reagent. This synthetic method has good prospects for the future large-scale production of single-crystalline β-$Co(OH)_2$ nanostructures owing to its high yield, low cost, and simple reaction apparatus. Ultra fine nanowires, nanowires with branched ultra fine nanoneedle (forest) and nanobelt with branched nanoneedles (pan trees) like structures of cobalt hydroxide are obtained with varying the ratio between supercritical water and triethylamine by 1:0, 2:1 and 1:2, respectively. The obtained morphologies are hexagonal phase of β-cobalt hydroxide with high crystallinity.

1. Introduction

One-dimensional (1D) nanoscale materials such as nanotubes, nanobelts, nanorods, and nanowires have been prepared by different approaches which can be classified into the following strategies [1,2]. First, the growth of 1D nanoscale materials is achieved in a hard template with well-confined structures, such as alumina, silica, block polymer, mica, and membranes [3,4]. Second, soft templates are used to produce 1D nanoscale materials [5,6]. Generally, in this process, surfactants are applied to stabilize the surface of nanonuclei and kinetically control the growth rates of various facets of nuclei. Third, the intrinsic structures are used to form 1D nanostructures [7,8]. Usually, the materials with hexagonal structure are favored to form 1D nanostructures under a suitable reaction condition. Fourth, vapor-liquid-solid (VLS) growth has been employed to prepare 1D nanostructures [9–11]. Recently, it was found that the low-temperature process based on one or more strategies described above is more promising to prepare 1D nanoscale materials.

Cobalt hydroxide has attracted increasing attention in recent years because of its novel electric and catalytic properties and important technological applications [12–15]. In particular, cobalt hydroxide can be used to enhance electrochemical performance when added to nickel oxyhydroxide electrodes by enhancing the electrode conductivity and chargeability [16]. It is well known that cobalt hydroxide has two polymorphs: α- and β-$Co(OH)_2$. These two phases are all-layered and have the same hexagonal structures, except that the β form is isostructural with brucite-like compounds and consists of a hexagonal packing of hydroxy ions with Co (II) occupying alternate rows of octahedral sites [17]. α-$Co(OH)_2$, however, is isostructural with hydrotalcite-like compounds that consist of stacked $Co(OH)_{2-x}$ layers intercalated with various anions in the interlayer space to restore charge neutrality. Synthesis of $Co(OH)_2$ with abundant morphologies via a facile route still remains a challenge. In this letter, we represent a new strategy to obtain a novel morphologies of $Co(OH)_2$ hydrothermally by the aid of supercritical water and triethylamine.

2. Experimental

2.1. Preparation

In a typical procedure, 1.5 g of Co powder and 0.5 g of triethyleamine were dissolved into the H_2O_2 under magnetic stirring. Different H_2O_2/triethyleamine molar ratios of 1:0, 2:1 and 1:2 were made. This alkaline solution was transferred into a Teflon-lined autoclave with about 50% capacity. The autoclave was then sealed and maintained at 200 °C for 24 h. After the reaction was completed, the precipitate was filtered, washed with distilled water and absolute ethanol for several times. Finally, the resulting product was dried in a vacuum at 60 °C for 3 h.

2.2. Measurements

The X-ray measurements were performed using Philips X'pert diffractometer supplied with copper X-ray tube ($\lambda_{k\alpha 1} = 1.5406$ A°), nickel filter, graphite crystal monochromator, proportional counter detector, divergence slit 1° and 0.1 mm receiving slit. The morphology

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doi:10.1016/j.matlet.2010.12.061