Structural and Morphological Properties of Nanosheet-like Structured Cobalt Hydroxide Films with Annealing Treatment

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ABSTRACT

Structural and morphological properties of cobalt hydroxide ($Co(OH)_2$) films prepared by a simple wet-chemical method were investigated with various annealing temperatures. The XRD and FTIR results confirmed that nanosheet-like structured $Co(OH)_2$ was synthesized at a temperature of 90 ºC and the phase transition to oxide occurred with annealing treatment.

1 Introduction

Hierarchical nanostructured transition metal hydroxides and oxides have been exclusively studied for their structural and morphological properties owing to their variation in optoelectronic and electrochemical applications, such as photovoltaic (PV) cells, light emitting diodes (LEDs), secondary batteries, supercapacitors, and oxygen evolution reaction (OER) catalysts [1-8]. The morphologies of nanostructured metal hydroxides have been reported to change from nanowires to nanowire-network structure with various preparation methods [4-7].

In our previous study, semi-transparent self-supporting nickel hydroxide ($Ni(OH)_2$) films were prepared using a simple wet-chemical method [9]. $Ni(OH)_2$ films were composed with nanosheet-like structures. Furthermore, the nanostructure of $Ni(OH)_2$ films could change from a nanosheet-like structure to a nanolayer-stacking structure with the incorporation of cobalt (Co) [10].

In this study, we investigated the effects of annealing treatment on the structural and morphological properties of cobalt hydroxide ($Co(OH)_2$) films prepared by a facile and cost-effective wet-chemical method at a relatively low growth temperature.

2 Experiment

To synthesize $Co(OH)_2$ nanostructures, an aqueous solution comprising cobalt acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$, 0.01 M) and hexamethylenetetramine (HMT, $C_6H_{12}N_4$, 0.01 M) was prepared. After stirring at room temperature for 1 h, the light pink-colored solution was stored in a dry oven at a temperature of 90 °C for 2 – 6 h. After centrifugation [9], the obtained samples were dried at 90 °C for 24 h, then annealed at 300 – 500 °C for 1 h in ambient air.

The crystal structures and phases of the nanostructured samples were investigated by X-ray diffraction (XRD). The chemical bonds and compositions were analyzed using Fourier-transform infrared (FTIR) spectroscopy. The morphology was examined using field emission scanning electron microscopy (FESEM).

3 Results and Discussion

Figure 1 shows the XRD patterns of the obtained samples without and with annealing treatment at 300 °C and 500 °C. Without annealing treatment, the diffraction peaks at 2θ positions of ~19.1° and ~38.6° could be indexed to the (001) and (002) planes of crystalline phased $Co(OH)_2$ (JCPDS card No.00-030-0443). With annealing treatment at a temperature of 300 °C, the diffraction peaks at 2θ positions of ~19.0°, ~36.8°, and ~38.6° could be indexed to the (111), (311), and (222) planes of crystalline phased cobalt oxide (Co_3O_4, JCPDS card No.00-042-1467). Intensities of these diffraction peaks slightly increased with increasing annealing temperature to 500 °C.

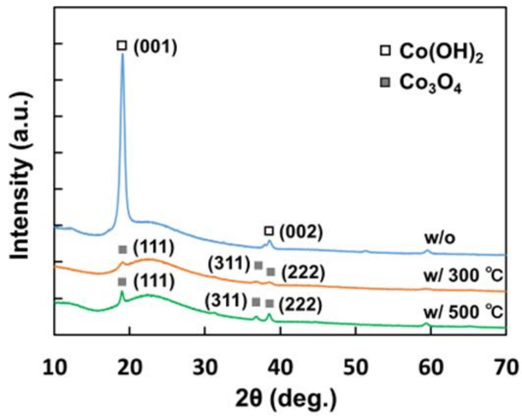

Fig.1. XRD patterns of obtained samples with various annealing treatment temperatures; Growth time was 6 h.

As shown in the FTIR spectra (Fig.2), without annealing treatment, strong absorption peaks at approximately 480 cm^{-1} and 3630 cm^{-1} were observed owing to the stretching vibration of the Co-OH bond and non-hydrogen bonded OH vibration, respectively [6]. A weak absorption at approximately 3400 cm^{-1} appeared owing to the stretching vibration band of OH [6]. Furthermore, it exhibited a stable hydroxide phase that was maintained at room temperature. With annealing treatment, strong absorption peaks at approximately 560 cm^{-1} and 670 cm^{-1} were observed owing to the Co-O stretching vibration modes [11]. From the XRD and FTIR results, it was confirmed that the obtained sample was $Co(OH)_2$ and the phase transition occurred from hydroxide to oxide with annealing treatment. In addition, the colors of the samples changed from white to dark gray during the phase transition.

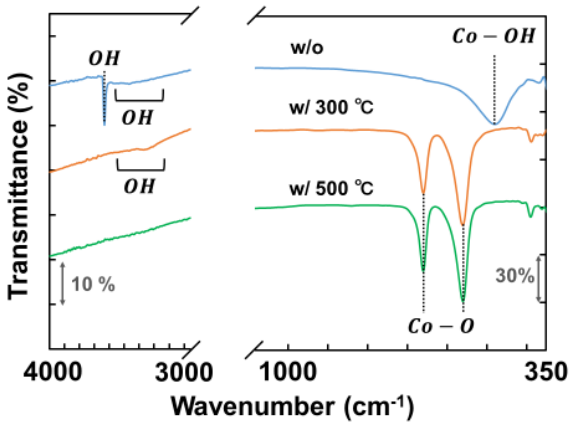

Fig.2. FTIR spectra of obtained samples with various annealing treatment temperatures; Growth time was 6 h.

Figure 3 shows the top and cross-sectional FESEM images of $Co(OH)_2$ nanostructured samples with various growth times and annealing treatment temperatures. After growth for 2 h (Fig.3(a)), nanosheet-like structures covered the surface. When the growth time increased to 6 h (Fig.3(b-d)), these morphological properties were well preserved. The nanosheet-like structures were interconnected, as shown in the cross-sectional FESEM image (Fig.3(c)). Several tens of nanometer-ordered nanosheet-like structures had an extremely smooth surface morphology, as shown in high-magnified FESEM image (Fig.3(d)). Nanosheet-like structures could provide advantages such as facile carrier transfer and transportation, and a large specific surface area [5,6]. Notably, the morphologies of $Co(OH)_2$ nanostructures were dependent on the cobalt precursors [8,12]. With aqueous solution of cobalt nitrate hexahydrate and HMT, the obtained $Co(OH)_2$ had the mixed structures of nanowires and nanosheets grown at 90 °C for 6 h. Furthermore, the morphologies of $Co(OH)_2$ nanostructures were effectively modified by varying the growth time, temperature, and HMT amount [8,12].

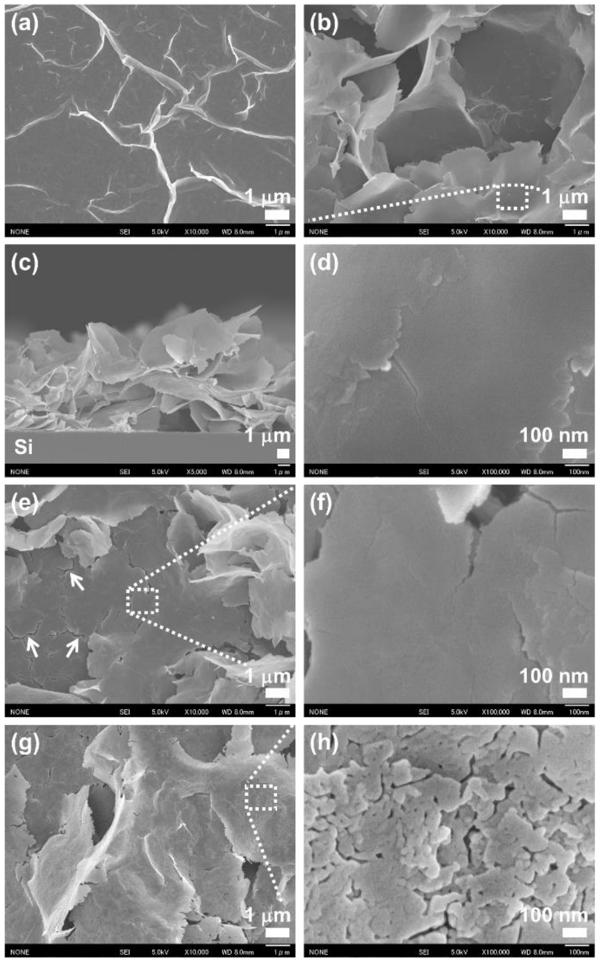

Fig.3. FESEM images of nanostructure samples with various growth times and annealing temperatures; (a) 2 h, without annealing treatment, (b-d) 6 h, without annealing treatment, (e,f) 6 h, with annealing at 300 °C, (g,h) 6 h, with annealing at 500 °C.

After annealing at 300 °C (Fig.3(e,f)), the smooth surface morphology was preserved; however, the cracks indicated by arrows appeared on the surface of nanosheet-like structures. When the annealing temperature increased to 500 °C (Fig.3(g,h)), the nanosheet-like structures were embedded with sub-level nanoparticles. In our previous study, similar surface morphological evolutions and phase transitions were observed on nanosheet-like structured $Ni(OH)_2$ with annealing treatment [9].

4 Conclusions

The $Co(OH)_2$ film was prepared by a simple wet-chemical method at a relative low growth temperature of 90 °C. It comprised several tens of nanometer-ordered nanosheet-like structures with a smooth surface morphology. After annealing treatment at a temperature of 300 °C, the phase transition was occurred from hydroxide to oxide and the morphological properties were well preserved. Then, the sub-level nanoparticles were observed on the surface of nanosheet-like structures with annealing treatment at a temperature of 500 °C.

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