Morphological Properties of Nickel-Cobalt Double Hydroxides Prepared by Facile Wet-Chemical Method

Kyung Ho Kim, Sena Motoyama, Maho Suzuki
Yoshio Abe, Midori Kawamura, Takayuki Kiba

Department of Materials Science and Engineering, Kitami Institute of Technology,
165 Koen-cho, Kitami, Hokkaido 090-8507, Japan
Keywords: $Ni(OH)_2$, $Co(OH)_2$, Nanosheet, Nanolayer

ABSTRACT

We synthesized nickel-cobalt double hydroxides (Ni-Co DHs) via a facile wet-chemical method at a relatively low reaction temperature and investigated their morphological properties with different Co precursors. With cobalt nitrate hexahydrate, the nanosheets were interconnected each other, while, the nanolayered structure was observed with cobalt acetate tetrahydrate.

1 INTRODUCTION

Recently, mixed metal double hydroxides (DHs) have been extensively studied in the field of optoelectronic applications due to their unique morphological properties [1-3]. Xie *et al.* synthesized nanoparticle structured cobalt nickel double hydroxides (Co_xNi_{1-x} LDHs) using cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), ammonium hydroxide ($NH_3{\cdot}H_2O$), and polyvinyl pyrrolidone (PVP) [1]. Zeng et al. reported excellent oxygen evolution reaction (OER) performance of Fe-Ni hydroxide nanosheets prepared via hydrothermal treatment on Fe-Ni alloy foam [2]. Abdolmohammad-Zadeh et al. reported the solid-phase extraction (SPE) sorbent performance of Ni-Al layered double hydroxide synthesized using nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), and NaOH [3]. In addition, Xu et al. prepared hierarchical mixed NiCu layered hydroxides nanowires on carbon fibre cloth and investigated their electrochemical performance with different molar ratio of Ni and Cu precursors, as ammonia fuel cells [4].

In our previous study, we synthesized zinc-aluminum layered double hydroxide (Zn-Al LDH) using aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_2{\cdot}9H_2O$), and hexamethylenetetramine (HMT, $C_6H_{12}N_4$). The Zn-Al LDH was composed of the hexagonal shaped nanosheets with diameter of 1-3 μm [5].

In this study, we investigated structural and morphological properties of Ni-Co DHs synthesized using mild condition at a relatively low reaction temperature of 90 ºC.

2 EXPERIMENT

2.1 Preparation Processes of Ni-Co DHs

To synthesis Ni-Co DHs, an aqueous solution of nickel acetate tetrahydrate (Ni(Ac), $Ni(CH_3COO)_2{\cdot}4H_2O$, 10 mM), cobalt nitrate hexahydrate (Co(NO), $Co(NO_3)_2{\cdot}6H_2O$, 10 mM), and hexamethylenetetramine (HMT, $C_6H_{12}N_4$, 10 mM) was prepared. After stirring at room temperature for 1 h, it was kept at 90 ºC for 4 h. The whitish powder sample was obtained by centrifugation. The detail preparation processes were described in our previous study [6]. The nanostructure samples were dried at 90 ºC for 24 h in air. For comparison, cobalt acetate tetrahydrate (Co(Ac), $Co(CH_3COO)_2{\cdot}4H_2O$, 10 mM) as cobalt precursor was used. The other processes were the same.

2.2 Characterization Methods

Crystal structure was measured using X-ray diffraction (XRD, D8 ADVANCE) with 0.02º/s step. Accelerated voltage and current were 40 V and 40 mA, respectively. Surface morphology was measured using field emission scanning electron microscopy (FESEM, JSM-6701F). Chemical bonds were characterized by Fourier transform infrared (FTIR, JASCO, FT/IR-6100) spectroscopy with a resolution of 8 cm^{-1}.

3 RESULTS & DISCUSSION

Figure 1 shows XRD pattern of nanostructure sample prepared with Ni(Ac) and Co(NO) precursors. The diffraction peaks at 2θ positions of ~11.2° and ~22.5° are indexed as the (003) and (006) planes of rhombohedral structured $Ni(OH)_2$, respectively (JCPDS card No.38-0715), respectively. In addition, the diffraction peaks at 2θ positions of ~19.3°, ~32.9°, and ~38.1° are indexed as the (001), (100), and (002) planes of hexagonal structured $Co(OH)_2$, respectively (JCPDS Card No. 30-0443).

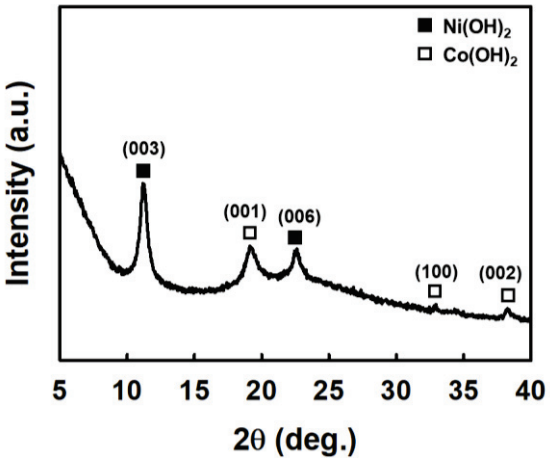

Fig.1. XRD pattern of Ni-Co DHs sample prepared with Ni(Ac) and Co(NO) precursors.

FTIR spectrum is shown in Fig.2. Absorption bands associated with the metal (Ni, Co)-OH bending vibrations are observed below 800 cm^{-1} [7]. Absorption bands are observed around 1300 ~ 1400 cm^{-1} due to NO_3^- and CO_3^{2-} from Ni and Co precursors [7]. Broad absorption band around 3400 cm^{-1} is originated to the stretching modes of OH bonded water molecules [7]. From XRD and FTIR results, it was well supported the formation of the Ni-Co DHs at a relatively low reaction temperature via a simple one-pot wet-chemical method.

Figure 3 show the top (a,b) FESEM images of Ni-Co DHs sample with Ni(Ac) and Co(NO) precursors. The nanosheets with micrometer-order length are interconnected each other. The thickness of the nanosheet is ~20 nm. Interestingly, the nanostructure sample synthesized using aqueous solution of Ni(Ac) and HMT had similar nanosheet structure. Also, it had the similar morphology obtained using aqueous solution of Co(NO) and

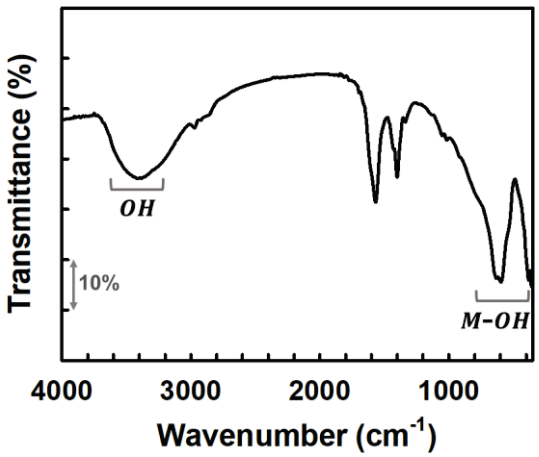

Fig.2. FTIR spectrum of Ni-Co DHs sample prepared with Ni(Ac) and Co(NO) precursors.

HMT. Furthermore, with annealing treatment at a temperature of 500 °C for 1 h in air ambient, the nanosheets were embedded with several nanometer order of nanoparticles. During annealing treatment, it could be due to evaporate H_2O, NO_3^-, and CO_3^{2-}, led to formation of the $NiCo_2O_4$ spinel oxide, which have potential as active electrode material for supercapacitor [8].

In case of the Ni-Co DHs directly grown on a fluorine-doped tin oxide (FTO) coated glass substrate, it had nanosheets structure, which vertically well aligned on the substrate. In a previous study, we study the electrochemical performances of entirely binder-free Ni-Co DHs compared with $Ni(OH)_2$ and $Co(OH)_2$. The thickness of individual nanosheets increased in order of $Ni(OH)_2$, Ni-Co DHs, and $Co(OH)_2$. The reversibility of the oxidation and reduction processes and rate capability of the Ni-Co DHs exhibited better than other samples. In addition, it had electrochromic performance. The color of the Ni-Co DHs changed from deep brownish in the oxidized state (@ 0.55 V vs Ag/AgCl) to pale brownish in the reduced state (@ -0.15 V vs Ag/AgCl). However, the cycling stability needs to be improved [9].

On the other hand, the nanostructure sample prepared with Ni(NO) and Co(Ac) as precursors, the light greenish-blue powder sample was obtained. It had a nanolayer-stacking structure (Fig.3(c)). The thickness of the individual nanolayer is around 100 nm. Similar morphology

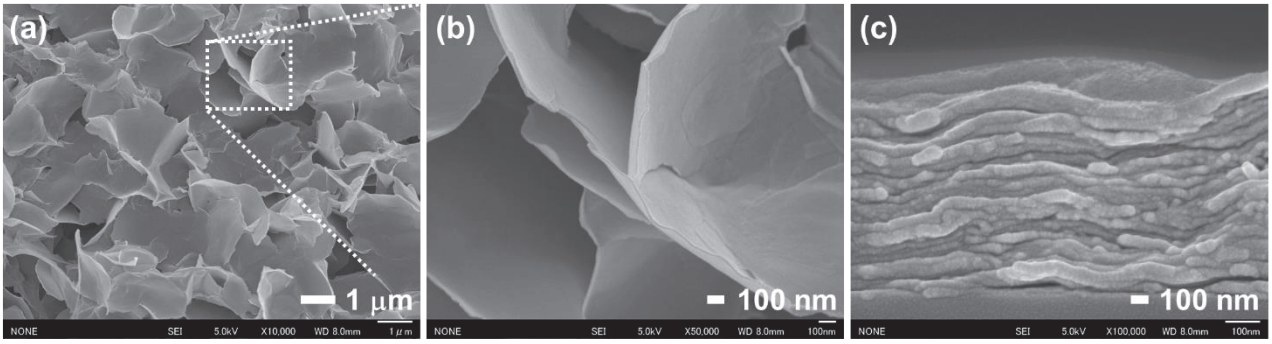

Fig.3. Top (a,b) and cross-sectional (c) FESEM images of Ni-Co DHs with different Co precursors; (a,b) Co(NO), (c) Co(Ac).

was observed on the $Ni(OH)_2$ nanostructure sample prepared with Cu incorporation [10].

4 CONCLUSIONS

Ni-Co DHs were synthesized by simple one-pot wet-chemical method with mild condition and investigated their morphological properties with different Co precursors. With Ni(Ac) and Co(NO) precursors, the nanosheet with thickness of the several nanometers scale was interconnected each other. However, the nanolayered structure was obtained with Ni(Ac) and Co(NO) precursors. It was effective way to tune the morphologies of the Ni-Co DHs using different precursors

REFERENCES

[1] L. Xie, Z. Hu, C.Lv, G. Sun, J. Wang, Y. Li, H. He, J. Wang, K. Li, "Co_xNi_{1-x} double hydroxide nanoparticles with ultrahigh specific capacitances as supercapacitor electrode materials," Electrochim. Acta, Vol. 78, pp. 205-211 (2012).

[2] L. Zeng, L. Yang, J. Lu, J. Jia, J. Yu, Y. Deng, M. Shao, W. Zhou, "One-step synthesis of Fe-Ni hydroxide nanosheets derived from bimetallic foam for efficient electrocatalytic oxygen evolution and overall water splitting," Chin. Chem. Lett., Vol. 29, pp. 1875-1878 (2018).

[3] H. Abdolmohammad-Zadeh, S. Kohansal, G.H. Sadeghi, "Nickel-aluminum layered double hydroxide as a nanosorbent for selective solid-phase extraction and spectrofluorometric determination of salicylic acid in pharmaceutical and biological samples," Talanta, Vol. 84, pp. 368-373 (2011).

[4] W. Xu, R. Lan, D. Du, J. Humphreys, M. Walker, Z. Wu, H. Wang, S. Tao, "Directly growing hierarchical nickel-copper hydroxide nanowires on carbon fibre cloth for efficient electrooxidation of ammonia," Appl. Catal. B Environ., Vol. 218, pp. 470-479 (2017).

[5] S. Motoyama, K.H. Kim, Y. Abe, M. Kawamura, T. Kiba, "Synthesis of zinc-aluminum layered double hydroxide and their structural properties," Proc. IDW'17, pp. 1405-1408 (2017).

[6] K.H. Kim, M. Mikami, Y. Abe, M. Kawamura, T. Kiba, "Morphological evolution of self-supporting nickel hydroxide nanostructures prepared by a facile wet-chemical method," Thin Solid Films, Vol. 654, pp. 49-53 (2018).

[7] Y. Yang, Y. Liang, Z. Zhang, Y. Zhang, H. Wu, Z. Hu, "Morphology well-controlled synthesis of NiO by solvothermal reaction time and their morphology-dependent pseudocapacitive performances," J. Alloy. Compd, Vol. 658, pp. 621-628 (2016).

[8] D. Yan, W. Wang, X. Luo, C. Chen, Y. Zeng, Z. Zhu, "$NiCo_2O_4$ with oxygen vacancies as better performance electrode material for supercapacitor," Chem. Eng. J., Vol. 334, pp. 864-872 (2018).

[9] K.H. Kim, S. Motoyama, Y. Abe, M. Kawamura, T. Kiba, "Comparative study on morphological and electrochemical properties of nickel-cobalt double hydroxide, cobalt hydroxide, and nickel hydroxide," J. Electron. Mater., Vol. 48, pp. 3000-3005 (2019).

[10] K.H. Kim, M. Mikami, Y. Abe, M. Kawamura, T. Kiba, “Structural and electrochemical properties of nanolayer-stacking structured copper-doped nickel hydroxide,” Int. J. Electrochem. Sci., Vol. 13, pp. 7655-7662 (2018).