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Preparation of self-assembled stacking of plates and hexagonal plates of β-cobalt hydroxides

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ABSTRACT

The self-assembled stacking of plates of β-cobalt hydroxides was synthesized with a cobalt-amine complex solution under microwave irradiation. Diethylenetriamine (DETA) was used to form the cobalt-amine complex. The cobalt-amine complex plays an important role in the formation of hierarchical stacking of plates of β-cobalt hydroxides. Single-crystal hexagonal plates of β-cobalt hydroxides were also prepared using a cetyl trimethyl ammonium bromide (CTAB) as a capping agent by a hydrothermal method and microwave method.

Key words : β-cobalt hydroxide, self-assembly, hexagonal plate, morphology

Introduction

The synthesis of unique morphologies of metal oxides and metal hydroxides has attracted significant attention due to the resulting novel structures, properties, and applications (1-3). Cobalt hydroxides have been widely used in electrochromic films and as an additive in nickel hydroxide electrode (4, 5). Many efforts have been devoted to the synthesis of cobalt hydroxides with various morphologies such as flower-like, hexagonal plates, and nanorods (6-10). Liu et al. reported the selective and controlled synthesis of single-crystal plates of β-cobalt hydroxides via homogeneous precipitation using hexamethylenetetramine as a hydrolysis agent (11). Sampanthar and Zeng synthesized the butterfly-like β-cobalt hydroxides with assistance of chelating agent ethylenediamine (12). In this paper, we report a simple method for controlled preparation of β-cobalt hydroxides with specific morphologies by hydrolysis using a diethylenetriamine (DETA) under microwave irradiation. The hydrothermal method was also used for preparing the hexagonal plates β-cobalt hydroxides using a cetyl trimethyl ammonium bromide (CTAB) as a capping agent.

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Experimental

$Co(CH_3COO)_2 \cdot 4H_2O$ (Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich), NaOH (Aldrich), DETA (Aldrich), and CTAB (Aldrich) were used as received. CTAB and DETA were used as a capping reagent and hydrolysis agent, respectively. We performed three different synthetic methods for preparing the β-cobalt hydroxides. The first method is the microwave irradiation technique with DETA. In this method, $Co(CH_3COO)_2 \cdot 4H_2O$ (5 mmol) and DETA (10 mmol) were dissolved in 100 mL of H_2O. This solution was put into a domestic microwave oven (Amana M84T, 2.45 GHz, 25 W). 100% of the output power of the microwave was used to irradiate a solution for 4 and 6 hr. The second method was the microwave irradiation technique with CTAB. Aqueous solution was prepared by adding 5 mmol CTAB to 20 mL of 5 mmol

$Co(NO_3)_2 \cdot 6H_2O$ ethanolic (ethanol:water = 1:1) solution. This solution was mixed with 50 mL of 10 mmol NaOH aqueous solution. A mixed solution was put into a microwave oven for 10 min. The third method is the hydrothermal technique with CTAB. The same solution as prepared by the second method was put into a Teflon-lined stainless autoclave at 120℃ for 3 hr. The β-cobalt hydroxide products were washed with water and ethanol several times, and then dried at 60℃ for 12 h in an oven.

The structures of the as-prepared β-cobalt hydroxide products were analyzed by powder X-ray diffraction (XRD, SIMENS Diffractometer D5000) with Cu Kα radiation. The morphologies of the as-prepared β-cobalt hydroxide products were characterized with scanning electron microscopy (SEM, Hitachi S-4300).

Results and Discussion

Fig 1 shows XRD patterns of α-cobalt hydroxide, β-cobalt hydroxide, and the as-prepared β-cobalt hydroxide products obtained by using DETA as a chelating and hydrolysis agent under microwave irradiation for 6 hr. Even XRD spectrum of the as-prepared β-cobalt hydroxide has large noise, XRD peaks of the as-prepared β-cobalt hydroxide products match with reported data of β-cobalt hydroxide (ICSD 10624). The β-cobalt hydroxide has a brucite-type structure with P3m1 space group. The cell parameters of β-cobalt hydroxide are a=b=3.19 Å, c=4.66 Å, α=β=90°, and γ=120°. Since no other peaks of impurities and α-cobalt hydroxide were detected, we concluded that β-cobalt hydroxide was successfully synthesized.

DETA is a water-soluble tridentate amine that can coordinate with Co^{2+} to form the cobalt-amine complex, $[Co(DETA)_2]^{2+}$. DETA also reacts with water to form the monohydrated DETA, $[DETAH]^+$, and OH^- due to the equilibrium process. Therefore, DETA can be also used as a hydrolysis agent. The cobalt-amine reacts with OH^- in solution under microwave irradiation to form $Co(OH)_2$ with the release of DETA. The possible chemical reactions producing $Co(OH)_2$ are as follows:

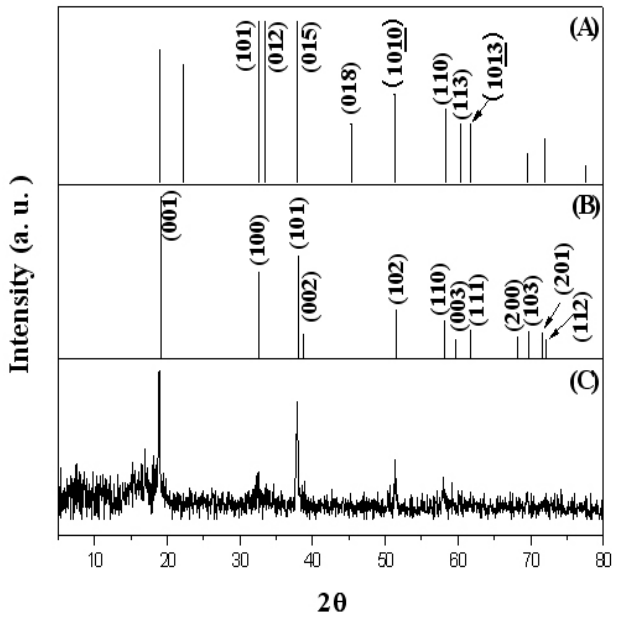

Fig 1. XRD patterns and Miller indices of (A) α-$Co(OH)_2$, (B) β-$Co(OH)_2$, and (C) β-$Co(OH)_2$ products obtained with DETA under microwave irradiation for 6 hr.

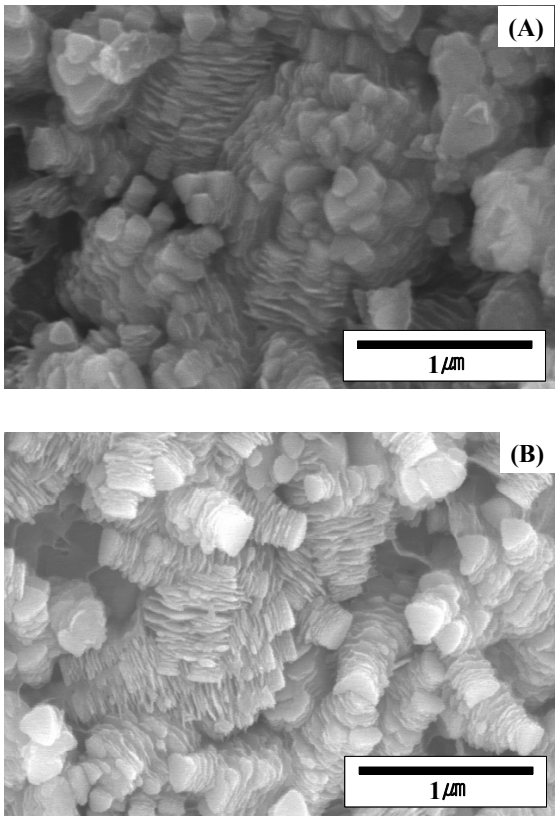

Fig 2. SEM images of the β-cobalt hydroxides products obtained with DETA under microwave irradiation for (A) 4 hr and (B) 6 hr.

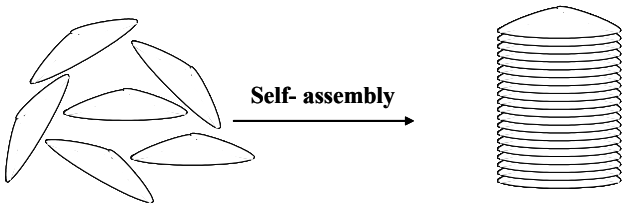

Fig 3. Diagram of self-assembly of quasi-triangular plate to form the hierarchical stacking of plates.

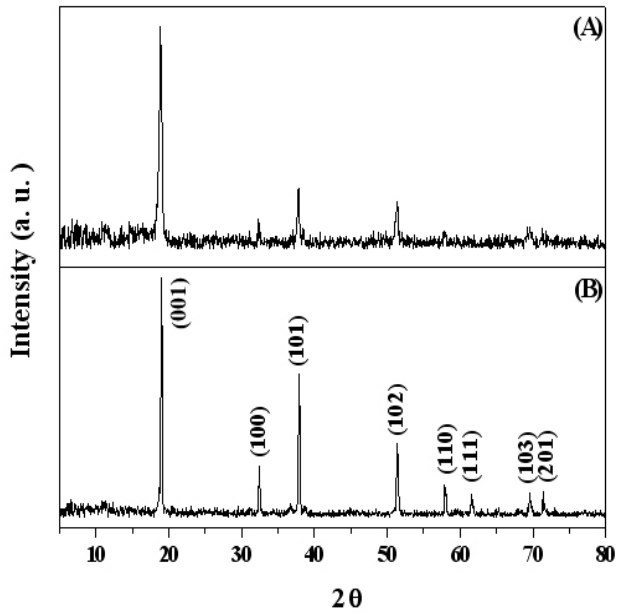

Fig 4. XRD patterns and Miller indices of β-$Co(OH)_2$ products obtained (A) under microwave irradiation for 10 min and (B) using an autoclave at 120℃ for 3 hr.

$$Co^{2+}\ (aq) + 2\ DETA \rightarrow [Co(DETA)_2]^{2+}\ (aq) \quad (1)$$

$$[Co(DETA)_2]^{2+}\ (aq) + 2\ OH^-\ (aq) \rightarrow Co(OH)_2 + 2\ DETA \quad (2)$$

Fig 2 shows SEM images of the β-cobalt hydroxides obtained with DETA under microwave irradiation for 4 and 6 hr. As the microwave irradiation time increases, the morphology of the β-cobalt hydroxide changes from simple aggregated plates to regular stacking of semi-triangular plates. The external shape of hierarchical microstructures resembles a stack of pancakes. In most systems, hierarchical assembly involves two distinct step. The first step is to synthesize the appropriate precursors, and the second step is to assemble the precursors into larger structures (13). It must have an enough time to assemble the precursors to form the hierarchical microstructures. DETA reacts with Co^{2+} to form the

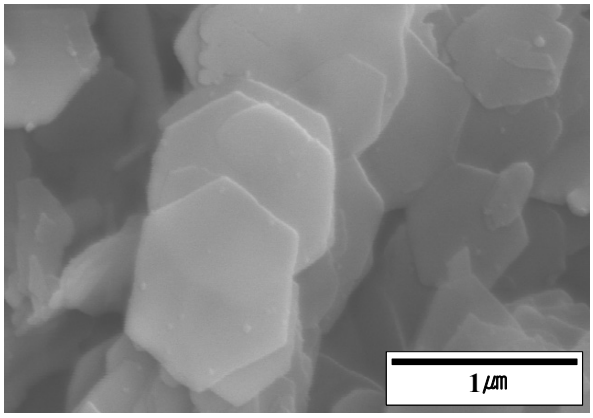

Fig 5. SEM image of the β-cobalt hydroxides products obtained by reacting $Co(NO_3)_2$ with NaOH and CTAB under microwave irradiation for 10 min.

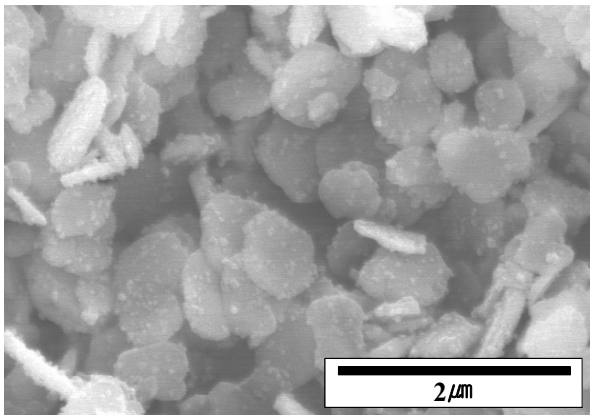

Fig 6. SEM image of the β-cobalt hydroxides products obtained by reacting $Co(NO_3)_2$ with NaOH and CTAB using an autoclave at 120℃ for 3 hr.

stable $[Co(DETA)_2]^{2+}$ complex. It retards the over-all formation reaction rate of β-cobalt hydroxide. Therefore the plates tend to self-assemble to reduce the surface energy and to form the hierarchical stacking of plates. The diagram of self-assembly of quasi-triangular plate to form the hierarchical stacking of plates is shown in **Fig 3**.

Fig 4 shows XRD patterns of the as-prepared β-cobalt hydroxides obtained from an mixed soltion of $Co(NO_3)_2 \cdot 6H_2O$, NaOH, and CTAB. Two different synthetic methods were used. In a microwave method, a solution was put into a microwave oven for 10 min. For the hydrothermal process, a solution was put into an autoclave at 120℃ for 3 hr. CTAB was used as a capping reagent to eliminate the hierarchical stacking behavior. No other peaks were detected, in-

dicating that these methods using microwave and hydrothermal processes yielded β-cobalt hydroxides free from impurities. In these cases, NaOH was used to hydrolysis the cobalt ions. The cobalt ions reacts directly with OH^- to form β-cobalt hydroxides very quickly. CTAB was used as a capping agent to eliminate the aggregation of β-cobalt hydroxides.

Fig 5 shows SEM image of the β-cobalt hydroxides under microwave irradiation for 10 min. The image consists of a large number of plates with a fairly uniform size. All of the plates has a regular hexagonal morphology with clean surfaces. The angles of adjacent edges is about 120°. The length of each side is 500 nm. The side-view image indicates that the thickness of hexagonal plate is approximately 50 nm. The aspect ratio is 10. In this synthetic method, NaOH was used to hydrolysis the cobalt ions. The formation reaction rate of β-cobalt hydroxides is very fast. Moreover, CTAB was used to prevent the β-cobalt hydroxide products from aggregating. Therefore, it had no enough time to form the self-assembled stacking of plates, single-crystalline hexagonal plates were only obtained.

Fig 6 shows SEM image of the β-cobalt hydroxides products obtained by reacting $Co(CH_3COO)_2$ with NaOH and CTAB using an autoclave at 120℃ for 3 hr. The SEM image is quite different that of products obtained by the microwave method. All of the plates have a blunted hexagonal morphology. The plates have rough surfaces with small nanoparticles. The length of each side is approximately 300 nm with 60 nm of thickness. Therefore, the aspect ratio is decreased compared to that of products obtained by the microwave method.

The crystal morphology is the equilibrium shape that results from the minimizing the anisotropic surface free energy. Fast crystal growth will occur in the direction perpendicular to the face with the highest surface energy (14). The layered hexagonal plates are lying on their {001} planes. The crystal growth perpendicular to {001} plane is faster than that along the along the <001> axis. Once the single-crystalline hexagonal plates is formed, it tends to form the self-assembled structures. The slow reaction rate plays an important role in formation of the self-assembled structures.

Conclusions

Uniform hexagonal plates of β-cobalt hydroxides were prepared by reaction of $Co(CH_3COO)_2$ with NaOH and CTAB. DETA was also used to hydrolysis and coordinate the cobalt ions. The stable $[Co(DETA)_2]^{2+}$ complex hinders the fast reaction of cobalt ion with OH^-. The self-assembled stacking of plates of β-cobalt hydroxides were obtained from the $[Co(DETA)_2]^{2+}$ complex solution.

References

(1) Li Y, Sui M, Ding Y, Zhang G, Zhuang J, Wang C (2000) Adv Mater **12**, 818
(2) Yang X, Makita Y, Liu ZH, Sakane K, Ooi K (2004) Chem Mater **16**, 5581
(3) Li XL, Liu JF, Li YD (2003) Mater Chem Phys **80**, 222
(4) Özer N, Chen DG, Büyüklimanli T (1998) Sol Energy Mater Sol Cells **52**, 223
(5) Li W, Zhang S, Chen J (2005) J Phys Chem B **109**, 14025
(6) Yang LX, Zhu YJ, Li L, Zhang L, Tong H, Wang WW, Cheng GF, Zhu JF (2006) Eur J Inorg Chem 4787
(7) Hou Y, Kondoh H, Shimojo M, Kogure T, Ohta T (2005) J Phys Chem B **109**, 19094
(8) Xu R, Zeng HC (2003) J Phys Chem B **107**, 12643
(9) Zhu Y, Li H, Koltypin Y, Gedanken A (2002) J Mater Chem **12**, 729
(10) Coudun C, Amblard E, Guihaumé J, Hochepied JF (2007) Catalysis Today **124**, 49
(11) Liu Z, Ma R, Osada M, Takada K, Sasaki T (2005) J Am Chem Soc **127**, 13869
(12) Sampanthar J, Zeng HC (2002) J Am Chem Soc **124**, 6668
(13) Song HC, Park SH, Huh YD (2007) Bull Kor Chem Soc **28**, 477
(14) Xu J, Xue D (2007) Acta Mater **55**, 2397

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