Electrochemical synthesis of cobalt hydroxide films with tunable interlayer spacings†

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An electrochemical synthetic condition is developed to produce cobalt hydroxide *films* with significantly increased basal spacings ($d_{001} \geqslant 25.0$ Å) by incorporating anionic surfactants (*i.e.* sodium dodecyl sulfate and 1-hexadecanesulfonate) into the interlayer regions *via* electrodeposition.

Cobalt hydroxides have received increasing attention due to their potential to be used as electrochemical supercapacitors, magnetic materials, and electrodes for batteries and electrochromic devices.[1–5] The structure of cobalt hydroxide is composed of two hydroxide layers sandwiching a Co^{2+} layer; the Co^{2+} ions occupy octahedral vacancies created by hexagonally packed OH^- ions. These two-dimensional $Co(OH)_2$ sheets are stacked to form a three-dimensional structure that is stabilized by hydrogen bonding between the layers.[6] When there are no ions or molecules stabilized in the interlayer region, cobalt hydroxide is isostructural with brucite and is formally known as β-$Co(OH)_2$.[7] The hydroxide layers can bear positive charges when the hydroxyl groups are partially protonated or additional Co^{2+} ions are introduced in interstitial sites. Such modification accompanies the incorporation of anions (and sometimes neutral molecules such as water) in the interlayer regions to stabilize the positively charged layers and maintain charge neutrality.[8,9] The resulting cobalt hydroxide structures possess significantly elongated basal spacings (d_{001}) compared to the β-phase. Direct substitution of hydroxide ions with bulkier anionic groups (*e.g.* nitrate, carboxylate) can also cause an elongation in basal spacing as in the case of the α-$Co(OH)_2$ phase in which hydroxyl groups are partially replaced by nitrate groups.[10]

Due to the layered feature, one of the main focuses of studying cobalt hydroxide has been introducing various organic and inorganic species in the interlayer regions in order to vary its basal spacings. This can considerably alter physical, chemical, and electrochemical properties of cobalt hydroxides by altering interlayer interactions. For example, the magnetic interactions between the Co-layers can diminish as the interlayer spacing increases, although this change does not affect the magnetic interactions within the layer, which may make it possible to produce multiple stacks of single layer magnets.[2,3]

To date, cobalt hydroxides with significantly elongated basal spacings have been prepared by introducing dicyanamide ($Co_5(OH)_8(C_2N_3)_2{\cdot}6H_2O$, d_{001} = 11.5 Å), suberate ($Co_5(OH)_8$–$(O_2CC_6H_{12}CO_2){\cdot}5H_2O$, d_{001} = 16.2 Å), caprylate ($Co_5(OH)_8$–$(C_7H_{15}CO_2)_2{\cdot}4H_2O$, d_{001} = 22.8 Å), dodecyl sulfate ($Co_5(OH)_8$–$(C_{12}H_{25}SO_4)_2{\cdot}(3H_2O{\cdot}2NH_3)$, d_{001} = 25.0 Å), and dodecyl benzene sulfonate ($Co_5OH_8(C_{18}H_{29}SO_3)_2{\cdot}6H_2O$, d_{001} = 30.2 Å) in the interlayer regions.[2,11] However, these phases were prepared not as thin films but as powders, which limits electrochemical characterizations or applications of these materials. Converting these powders to film-type electrodes may not be feasible because cobalt hydroxide may decompose during the annealing processes (decomposition temperature = 168 °C), which is required to achieve good electrical continuity between the particles and the substrate.

In this study, we report a facile one-step electrochemical synthesis for the preparation of thin $Co(OH)_2$ *films* with significantly increased basal spacings ($d_{001} \geqslant 25$ Å). This method incorporates anionic surfactant molecules (*e.g.* sodium dodecyl sulfate (SDS), 1-hexadecanesulfonate sodium salt (SHDS)) from the plating medium between the cobalt hydroxide layers as spacers during the electrodeposition process. The method described here may be used as a general and facile route to prepare a variety of inorganic layered materials (*e.g.* layered double hydroxides (LDH), layered sulfides) as thin-film type electrodes with tunable basal spacings.

$Co(OH)_2$ films are cathodically deposited from a nitrate bath by reduction of nitrate ions ($NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ E_o = 0.01 V *vs.* NHE). The generation of OH^- at the working electrode increases the local pH and provides for the deposition of $Co(OH)_2$.[8,12] For our purpose of increasing the interlayer spacing of $Co(OH)_2$, 0.01 wt% of SDS was added to the 0.02 M cobalt nitrate solution used as a plating medium. Electrodeposition was carried out potentiostatically (constant potential deposition) at 75 °C and −0.5 V against an Ag/AgCl in 4 M KCl reference electrode. The counter electrode was prepared by sputter coating 100 Å of titanium followed by 500 Å of platinum on clean glass slides. The working electrode was prepared by depositing 100 Å of chromium followed by 500 Å of gold on clean glass slides by thermal evaporation.

The X-ray diffraction pattern (XRD) of the resulting $Co(OH)_2$ film is shown in Fig. 1. While β-$Co(OH)_2$ possesses a basal spacing of 4.6 Å, our films show a considerable increase in basal spacing (d_{001} = 25 Å) due to the incorporation of SDS into the interlayer region. The basal spacing observed in our $Co(OH)_2$–SDS films is identical to that of $Co(OH)_2$ films prepared by a chemical precipitation method where OH^- groups are partially replaced by SDS.[2] The expansion of the interlayer spacing caused by the introduction of SDS molecules appears to interfere with long-range ordering along the *a*- and *b*-axes, and no well defined *hk0* reflections were observed. When the deposition potential became more negative than −0.5 V (equivalent to increasing

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† This paper is dedicated to the memory of Professor Ian P. Rothwell.

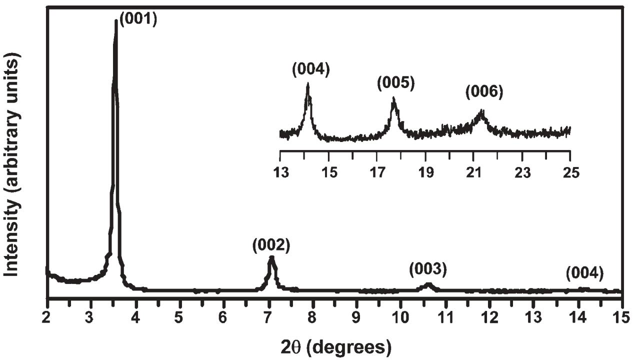

Fig. 1 X-Ray diffraction pattern of $Co(OH)_2$ films deposited with 0.01 wt% SDS on a Au electrode (Cu K_α radiation, $\lambda = 1.54$ Å). The inset shows high order 00*l* peaks.

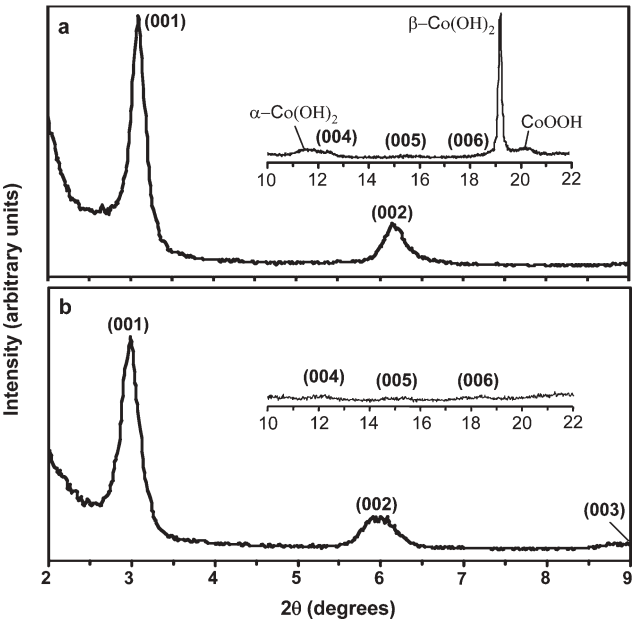

Fig. 2 X-Ray diffraction patterns of (a) $Co(OH)_2$ films deposited on a Au electrode from an aqueous solution containing 0.01 wt% SHDS and (b) $Co(OH)_2$ films deposited from an EG solution (H_2O(vol) : EG(vol) = 1 : 1) containing 0.05 wt% SHDS. The inset shows wide angle XRD patterns (Cu K_α radiation, $\lambda = 1.54$ Å).

overpotential), the XRD pattern from the $Co(OH)_2$–SDS phase shows reduced intensities, and side products consisting of β-$Co(OH)_2$ and α-$Co(OH)_2$ appeared.

Energy dispersive spectroscopy (EDS) of our $Co(OH)_2$–SDS films shows a Co to S atomic ratio of 1 : 0.2, indicating that approximately 10% of OH^- groups are replaced by SDS ($Co(OH)_{1.8}SDS_{0.2}$). The Co to S ratio remains the same when the amount of SDS in the plating medium increases from 0.01 wt% to 1.0 wt%. This indicates that there is an optimum amount of SDS that can be incorporated within the $Co(OH)_2$ structure and that 0.01 wt% of SDS (0.35 mM SDS) in the plating medium was enough to achieve this composition (the Co to S molar ratio in the plating medium is 1 : 0.00173). Using such a dilute solution for high quality manipulation of basal spacing is possible only because electrodeposition occurs at solid–liquid interfaces where the local concentration of surfactant molecules is significantly higher than that in the bulk solution due to surface forces.[13,14] This result clearly suggests that electrodeposition can provide a facile and efficient route to prepare $Co(OH)_2$ films with tunable interlayer spacings.

Further enhancement of the cobalt hydroxide basal spacing was accomplished by adding 0.01 wt% SHDS (0.305 mM) which has longer carbon chains than SDS. The XRD pattern of the $Co(OH)_2$ films deposited at 75 °C and −0.5 V shows that the basal spacing is indeed increased to $d = 28$ Å (Fig. 2(a)). However, the wide angle XRD of this film shows the presence of impurities that are identified as β-$Co(OH)_2$, α-$Co(OH)_2$ and CoOOH. These impurities could not be eliminated by tuning deposition conditions alone (*e.g.* deposition temperature, deposition potential/current). Our attempt to increase the purity of the $Co(OH)_2$–SHDS phase by adding more SHDS to the plating medium also failed due to the extremely low solubility of SHDS in an aqueous solution. Therefore, in order to increase the solubility of SHDS, we introduced 50 vol% of ethylene glycol (EG) to the plating medium. When 0.05 wt% of SHDS was dissolved in the EG solution, the impurity phases were successfully removed and a pure $Co(OH)_2$–SHDS phase was obtained (Fig. 2(b)). The optimum deposition potential to obtain the $Co(OH)_2$–SHDS phase was −0.6 V. The basal spacing of $Co(OH)_2$–SHDS obtained in the EG solution is slightly larger ($d_{001} = 29$ Å) than that obtained from aqueous media, indicating that introducing co-solvents may also be used to finely tune the interlayer spacings. The EDS analysis of the pure $Co(OH)_2$–SHDS film shows the identical Co to S atomic ratio observed in the $Co(OH)_2$–SDS film.

The scanning electron micrographs (SEM) of β-$Co(OH)_2$ films and $Co(OH)_2$ films containing SDS and SHDS show a clear morphological difference (Fig. 3(a)–(c)). While β-$Co(OH)_2$ films contain hexagonal plates with well defined crystal facets and edges, $Co(OH)_2$ films containing SDS and SHDS show amorphous features absent of well-developed crystal shapes. Transmission

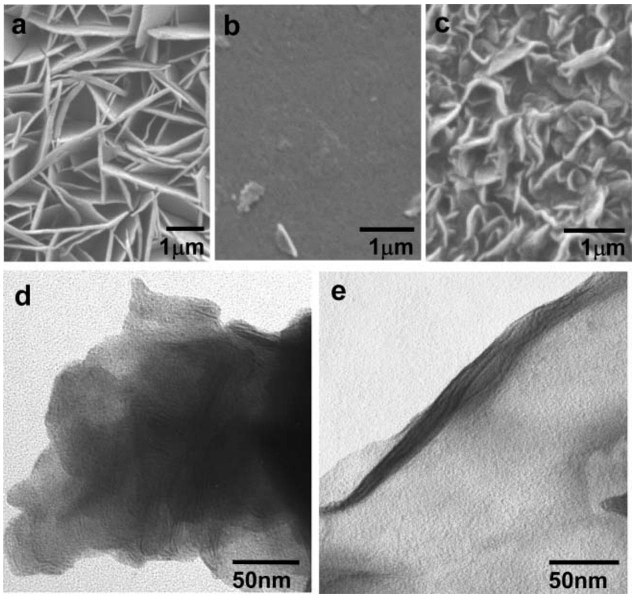

Fig. 3 SEM images of (a) β-$Co(OH)_2$ film and $Co(OH)_2$ films containing (b) SDS and (c) SHDS; TEM images of $Co(OH)_2$ films containing (d) SDS and (e) SHDS.

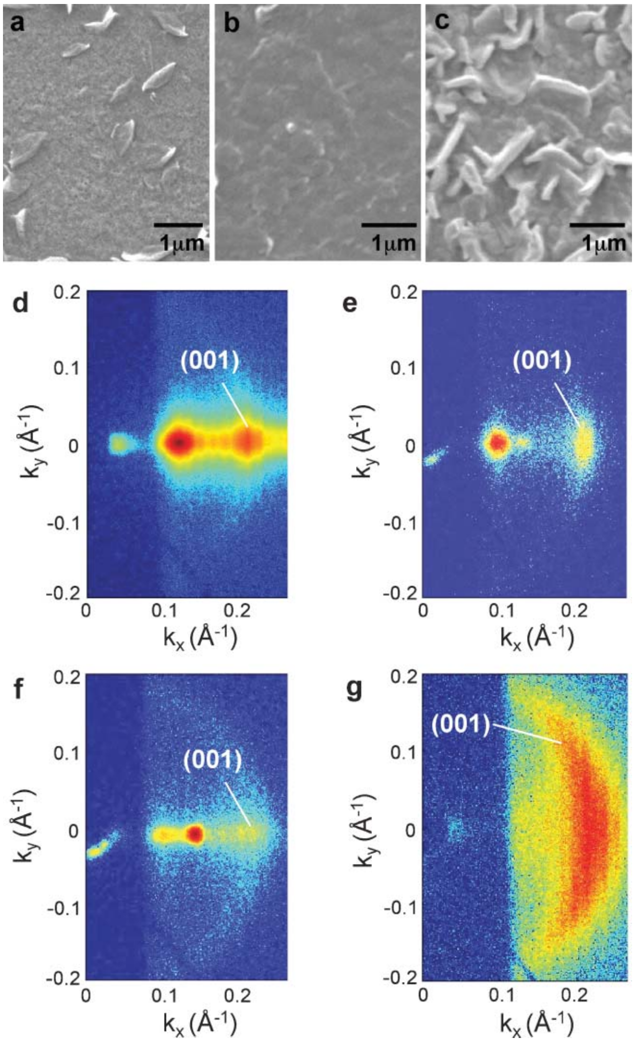

Fig. 4 SEM images of $Co(OH)_2$–SDS films deposited on (a) Pt, (b) Pd and (c) FTO substrates; 2D gi-SAXS patterns of $Co(OH)_2$–SDS films deposited on (d) Au, (e) Pt, (f) Pd and (g) FTO substrates. The reflections present between the incident beam ($k_x = k_y = 0$; $k = 2\pi/d$) hidden by the beam stop and (001) reflections are artifacts associated with reflections from the substrates.[15]

electron micrographs (TEM) of $Co(OH)_2$ films containing SDS and SHDS are shown in Fig. 3(d) and (e) in which the lamellar features are evident along the fringes of the layers.

The effect of substrate on the formation of $Co(OH)_2$–SDS phases was also studied by changing the type of working electrodes (*e.g.* Au, Pt, Pd, and fluorine doped tin oxide (FTO)). The $Co(OH)_2$–SDS films deposited on these substrates show the same d_{001} values confirmed by XRD patterns. However, the type of substrate affected the micro-level morphologies of films and therefore the stacking directions of lamellar layers relative to the substrates, which can be probed by 2D grazing incidence small angle X-ray scattering (2D gi-SAXS).

SEM studies show that the surface morphologies of $Co(OH)_2$–SDS films deposited on the Pd and Pt substrates look similar to that of films deposited on the Au substrate, which is smooth and flat (Fig. 4(a–b)). The gi-SAXS patterns of the films deposited on Au, Pt, and Pd substrates commonly show an array of horizontally aligned discrete spots, which indicates that the $Co(OH)_2$ layers in these films are stacked parallel to the substrates (Fig. 4(d–f)). However, the $Co(OH)_2$–SDS film deposited on the FTO substrate shows a relatively rough surface containing multiple randomly oriented domains (Fig. 4(c)). Indeed, the gi-SAXS pattern of this film shows arc-shaped scattering patterns, indicating that the $Co(OH)_2$–SDS film contains various lamellar domains with a wide distribution of the stacking directions (Fig. 4(g)). These structural details may become important features that need to be precisely tuned when constructing electrochemical devices.

In summary, we demonstrated the possibility of producing $Co(OH)_2$ films with tunable interlayer spacings *via* electrodeposition by incorporating long chain surfactant molecules into the interlayer regions. Due to the interfacial aggregation phenomena of amphiphiles used as spacers, high quality manipulation of basal spacing was achieved using extremely dilute surfactant solutions (0.01–0.05 wt%). By changing the type of working electrode, micro-level morphologies of the films and the stacking directions of $Co(OH)_2$ layers could also be altered, which provides an additional freedom in assembling lamellar structured films. We are currently extending this method to the production of various LDH materials as thin-film type electrodes with variable interlayer spacings to investigate optimum structures to assemble (electro)-chemical sensors.

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15 2D gi-SAXS patterns were obtained using a Molecular Metrology diffractometer with pinhole collimated Cu K_α radiation. The sample-to-detector distance was 484 mm and the data was acquired at an angle of incidence of 1.2°.