

Electronic Supplementary Information (ESI)

Selective Synthesis and Thin-Film Formation of α -Cobalt Hydroxide through an Approach Inspired by Biomineralization

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Experimental Procedure

Synthesis of α -Co(OH)₂: The precursor solutions containing cobalt chloride hexahydrate (CoCl₂·6H₂O 10 or 20 mM; Kanto, 99.0 %) were prepared with purified water at room temperature. Aqueous solutions of ammonia (NH₄OH, approximately 28 wt.%) were diluted by 2 or 5 wt.%. Two glass bottles each containing 20 mL of the precursor solution were put in a vessel (700 mL) with the two sample bottles each containing about 5 mL of the ammonia solution. The precipitates in Figure 1 were prepared by the solutions containing 10 mM of CoCl₂·6H₂O and 2 wt.% of NH₄OH. The precipitates were collected by centrifugation and then were dried at room temperature. For the thin-film formation, the solid organic matrices were immersed in the solutions containing 10 mM of CoCl₂·6H₂O with 2 wt.% of NH₄OH. The thin films of the nanosheets were obtained with addition of poly(acrylic acid) (Aldrich, $\overline{M}_w=2 \times 10^3$, 1.5 $\times 10^{-3}$ wt.%) in the precursor solution containing cobalt ions. The resultant thin films were rinsed by purified water and were dried at room temperature.

Preparation of the solid organic matrices: Chitosan (Wako Chemical) and polyaniline (emeraldine base, $\overline{M}_w=1 \times 10^4$, Aldrich) were used without further purification. Chitosan (1 wt.%) was dissolved in purified water containing 1 wt.% acetic acid. A chitosan matrix was

prepared by spin coating of the solution onto a glass substrate with a spinning rate of 4000 rpm for 60 sec. Polyaniline (1 wt.%) was dissolved in dimethylformamide. The remaining polyaniline was removed by the filtration. The solution was coated on a glass substrate with a spinning rate of 800 rpm for 60 sec. Then, these substrates were heated at about 130 °C for 1 hour to remove the solvents.

Characterization: The morphologies of the resultant materials were observed by a field emission SEM (Hitachi, S-4700 operated at 2.0 kV). The crystal structures and orientation were analyzed by TEM (JEOL, JEM-2010HC operated at 200 kV) and XRD (Rigaku, RINT-2400 with $\text{CuK}\alpha$ radiation). For the electron microscope analyses, the conductive treatments were not performed.

Explanations for the Structures of Low Crystalline $\alpha\text{-Co(OH)}_2$

In the main text, we describe that the XRD pattern of the low crystalline $\alpha\text{-Co(OH)}_2$ only shows the (003), (006), (100), and (110) planes (around explanations about Fig. 1c). Cobalt hydroxide is the layered structure of the two-dimensional monolayers consisting of edge-shared $\{\text{CoO}_6\}$ octahedrons. The disordered stacking of the monolayers in the c axis direction results in the formation of the low crystalline structures exhibiting such XRD pattern.

The thin films formed on the chitosan matrix

The SEM images indicate that the hexagonal plates of $\text{Co}(\text{OH})_2$ crystals are formed parallel to the chitosan matrices.

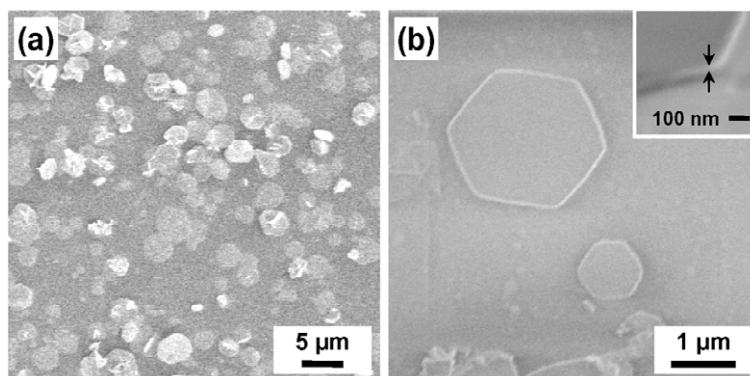


Fig. S1 SEM images of the thin films formed on the chitosan matrices. The inset in panel (b) shows the thickness of crystals.

The deposition on a glass substrate

The SEM images suggest that the plates of $\text{Co}(\text{OH})_2$ crystals are deposited on a bare glass substrate without a specific crystallographic orientation.

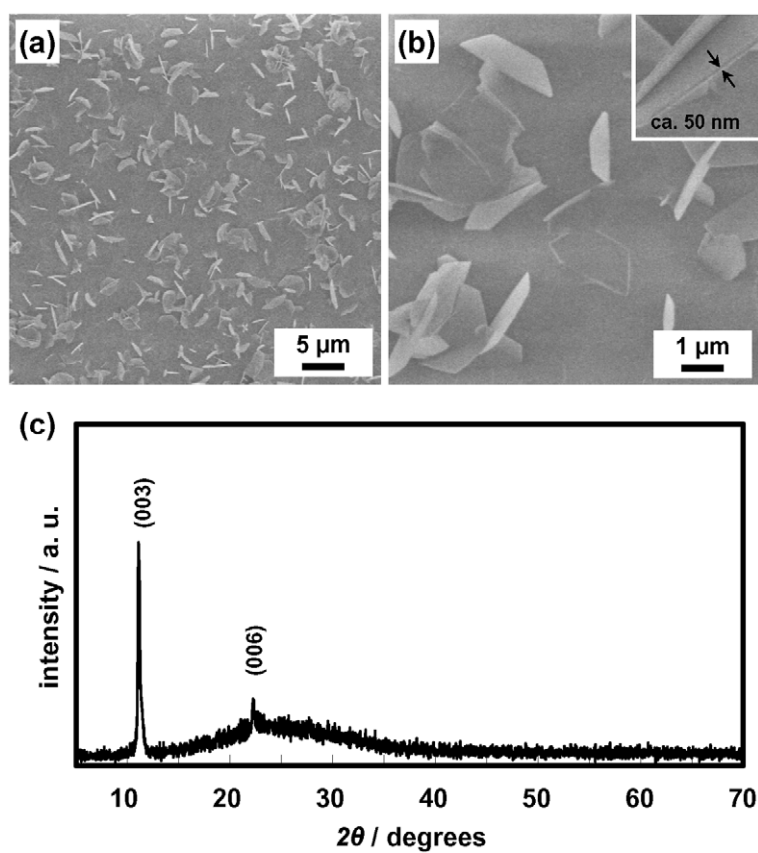


Fig. S2 SEM images (a,b) and XRD pattern (c) of the deposits on a glass substrate. The inset in panel (b) shows the thickness of crystals deposited on a glass substrate.

The orientation of the thin films formed on the chitosan matrix

In addition to the SEM images, the XRD patterns also support that the *c* axes of the α -Co(OH)₂ are oriented perpendicular to the chitosan matrices.

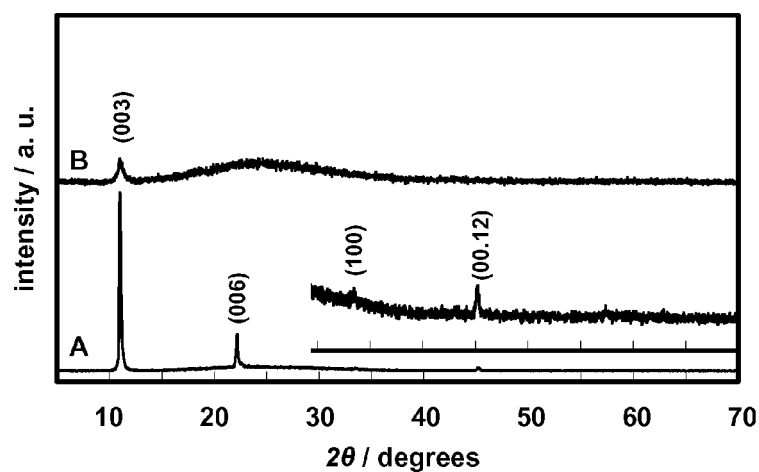


Fig. S3 XRD patterns of the thin films formed on the chitosan matrices in the absence (A) and presence (B) of PAA.

The deposit on a glass substrate in the presence of PAA

We could not find the film formation on a bare glass substrate when PAA is added in the precursor solution. A small amount of crystals is observed on the SEM images.

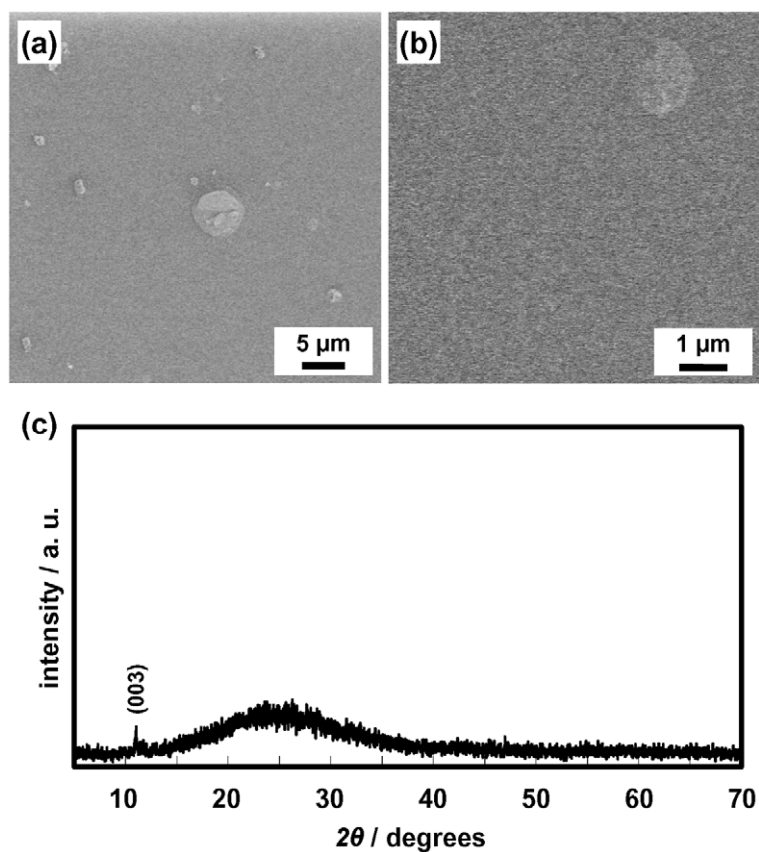


Fig. S4 SEM images (a,b) and XRD pattern (c) of the deposits on a glass substrate in the presence of PAA.

The single crystalline structures of α -Co(OH)₂ hexagonal plates and nanosheets

The nanocrystals are not observed in the hexagonal plates and nanosheets deposited on the matrices. The results suggest that these crystals are not mesocrystals but single crystalline structures.

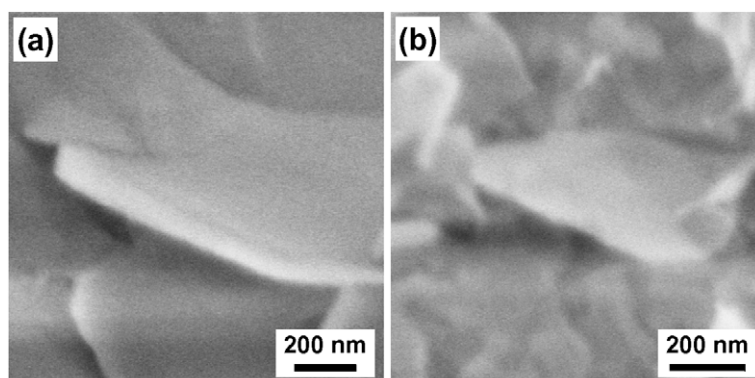


Figure S5. Magnified SEM images of the α -Co(OH)₂ hexagonal plates and nanosheets deposited on polyaniline matrices without (a) and with (b) PAA.