Electronic Supplementary Information

Synthesis and characterization of water-swellable LDH (layered double hydroxide) hybrids containing a sulfonate-type intercalant

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S-1. Preparation of starting LDHs

(a) MgAl-LDH3

ClO_4^-MgAl-LDH3 was used for the anion exchange by the sulfonates. To obtain ClO_4^-LDH, two methods were used as described below using commercially available CO_3^{2-}MgAl-LDH3 as the starting material:

Method 1: 50 mL of 0.1 M acetate buffer/ $NaClO_4$ mixed solution with AcOH ratio ([AcOH]/([AcOH]+[AcONa])) = 0.127 and $NaClO_4$ concentration = 2 M was added to CO_3^{2-}MgAl-LDH3 (100 mg). Under N_2 flow (500 mL·min^{-1}), the obtained suspension was stirred for 18 h at room temperature (~25 °C). The resulting product was filtered, washed with degassed and deionized water and vacuum-dried to yield ClO_4^-MgAl-LDH3 (108 mg) as a white powder.

Method 2: A solution prepared by diluting 60% perchloric acid (350 mg; 2.09 mmol as $HClO_4$) with 5 mL methanol was added dropwise to a suspension of CO_3^{2-}MgAl-LDH3 (500mg; 1.66 mmol based on formula (2) in the text) in 45 mL methanol under N_2 flow (500 mL·min^{-1}), and under vigorous stirring. The mixed suspension was stirred for 1 h at room temperature under N_2 flow. The resulting suspension was filtered, washed with methanol and vacuum-dried to yield white powder of ClO_4^-MgAl-LDH3 (561 mg). Detailed explanation on this method is given in S-1 (c).

(b) MgAl-LDH2s

ClO_4^-MgAl-LDH2 was used for the anion-exchange by organic sulfonates. ClO_4^-MgAl-LDH2 was derived from CO_3^{2-}MgAl-LDH2 prepared by the homogeneous precipitation method.

CO_3^{2-}MgAl-LDH2 was prepared as follows: A mixed solution (25 mL) of $MgCl_2 \cdot 6H_2O$ (508 mg), $AlCl_3 \cdot 6H_2O$ (302 mg), and HMT (613 mg) (Mg/Al = 2.0; [Mg+Al] = 0.15 M; HMT = 3.5 × [Al]) was prepared and, after filtration using a membrane filter (0.2 μm, Millipore), the solution was placed in a 50-mL Teflon® inner vessel within a stainless steel outer vessel (San'ai Kagaku). The mixture was allowed to react at 140 °C for 24 h under air-tight conditions. The resulting product was filtered, washed and vacuum-dried to yield CO_3^{2-}MgAl-LDH2 (279 mg) in white powder state.

ClO_4^-MgAl-LDH2 was prepared using method 2 described above. A solution of 5 mL methanol with 60% perchloric acid (175 mg) was added dropwise to a suspension of CO_3^{2-}MgAl-LDH2 (202 mg) in 45 mL methanol under N_2 flow

(500 mL·min^{-1}) and vigorous stirring. The mixed suspension was further stirred for 1 h at room temperature under N_2 flow. The resulting suspension was filtered, washed with methanol, and vacuum-dried to yield white powder of ClO_4^- MgAl-LDH2 (238 mg).

(c) About the decarbonation method using $HClO_4$/ methanol

This is a variation of acid decarbonation method, but, by using methanol, the dissolution of LDH was drastically suppressed and reaction proceeded almost quantitatively without addition of salt. The optimum mol ratio (*f*) of H^+ in $HClO_4$ and CO_3^{2-} in LDH (*i.e.*, $f = [H^+]/(2\times[CO_3^{2-}])$) was 1.25 ~ 2.0 (see Fig. S-1). As shown in the figure, for methanol solvent, weight loss is negligible and Mg/Al ratio did not change (from analysis data) even if $HClO_4$ was added up to $f = 8$. FTIR spectra showed that full decarbonation was attained in methanol at far less $HClO_4$ addition, $f = 1.25$. Full decarbonation means complete conversion into ClO_4^-LDH with no remaining CO_3^{2-}. On the contrary, if water is used instead of methanol, $HClO_4$ should be added more than $f = 3$ for complete decarbonation, but weight loss due to LDH dissolution was found more than 20% at $f = 3$. In the figure, weight increase up to $f = 1$ is observed. This is due to the molecular weight change from CO_3^{2-} to ClO_4^-LDH.

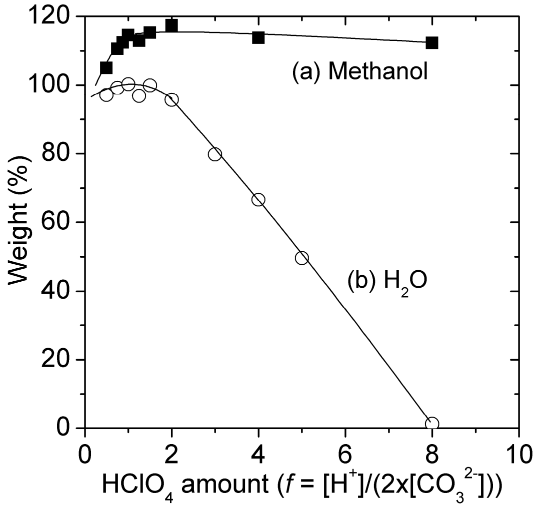


Fig. S-1. Weight change of CO_3^{2-}MgAl-LDH3 by the action of $HClO_4$ in (a) methanol and (b) water. The amount of $HClO_4$ was varied.

S-2. Synthetic conditions of various LDHs other than MgAl-LDHs.

(a) Preparation of CO_3^{2-} and ClO_4^-NiAl-LDH2

The typical synthesis process of CO_3^{2-}NiAl-LDH2 was as follows: 12.5 mL of mixed solution of $Ni(NO_3)_2·6H_2O$ (364 mg), $Al(NO_3)_3·9H_2O$ (235 mg), and HMT (307 mg) (Ni/Al = 2.0; [Ni+Al] = 0.15 M; HMT = 3.5 × [Al]) was placed in a 25-mL Teflon® inner vessel within a stainless steel outer vessel (San'ai Kagaku). The mixture was allowed to react at 180 °C for 3 days under air-tight conditions. The resulting product was filtered, washed and vacuum-dried to yield CO_3^{2-}MgAl-LDH2 (185 mg) as greenish blue powder.

ClO_4^-NiAl-LDH2 was prepared by using the method 2 process described for MgAl-LDHs. A solution prepared by adding 5mL methanol to 60% perchloric acid (105 mg) was added to a suspension of CO_3^{2-}NiAl-LDH2 (155 mg) in 45mL methanol in dropwise under N_2 flow (500 mL·min^{-1}), and under vigorous stirring. The mixed suspension was stirred for 1 h at room temperature under N_2 flow. The resulting suspension was filtered, washed with methanol and vacuum-dried to yield greenish blue powder of ClO_4^-NiAl-LDH2 (180 mg).

(b) Preparation of CO_3^{2-} and ClO_4^-NiAl-LDH3

CO_3^{2-}NiAl-LDH3 was prepared as follows: 12.5 mL of mixed solution of $Ni(NO_3)_2·6H_2O$ (409 mg), $Al(NO_3)_3·9H_2O$ (176 mg), and Urea (254 mg) (Ni/Al = 3.0; [Ni+Al] = 0.15 M; Urea = 9 × [Al]) was placed in a 25-mL Teflon® inner vessel within a stainless steel outer vessel (San'ai Kagaku). The mixture was allowed to react at 180 °C for 3 days under air-tight conditions. The resulting product was filtered, washed and vacuum-dried to yield CO_3^{2-}NiAl-LDH3 (188 mg) in greenish blue powder state.

By using the method 2 process described above, ClO_4^-NiAl-LDH3 was prepared. A solution prepared by adding 5 mL methanol to 60% perchloric acid (140 mg) was added to a suspension of CO_3^{2-}NiAl-LDH3 (268 mg) in 45mL methanol in dropwise under N_2 flow (500 mL·min^{-1}), and under vigorous stirring. The mixed suspension was stirred for 1 h at room temperature under N_2 flow. The resulting suspension was filtered, washed with methanol and vacuum-dried to yield greenish blue powder of ClO_4^-NiAl-LDH3 (297 mg).

(c) Preparation of CO_3^{2-} and ClO_4^-NiAl-LDH4

CO_3^{2-}NiAl-LDH4 was prepared as follows: 12.5 mL of mixed solution of $Ni(NO_3)_2·6H_2O$ (436 mg), $Al(NO_3)_3·9H_2O$ (141 mg), and Urea (248 mg) (Ni/Al = 4.0; [Ni+Al] = 0.15 M; Urea = 11 × [Al]) was placed in a 25-mL Teflon® inner vessel within a stainless steel outer vessel (San'ai Kagaku). The mixture was allowed to react at 180 °C for 3 days under air-tight conditions. The resulting product was filtered, washed and vacuum-dried to yield CO_3^{2-}NiAl-LDH3 (223 mg) as greenish blue powder.

By using the method 2 process described above, ClO_4^-NiAl-LDH4 was prepared. A solution prepared by adding 5 mL methanol to 60% perchloric acid (140 mg) was added to a suspension of CO_3^{2-}NiAl-LDH4 (329 mg) in 45mL methanol in dropwise under N_2 flow (500 mL·min^{-1}), and under vigorous stirring. The mixed suspension was stirred for 1 h at room temperature under N_2 flow. The resulting suspension was filtered, washed with methanol and vacuum-dried to yield greenish blue powder of ClO_4^{-}NiAl-LDH4 (353 mg).

(d) Preparation of CO_3^{2-} and Cl^{-}CoAl-LDH2

CO_3^{2-}CoAl-LDH2 was prepared as follows: 25 mL of mixed solution of $CoCl_2 \cdot 6H_2O$ (238 mg), $AlCl_3 \cdot 6H_2O$ (121 mg), and Urea (300mg) (Co/Al = 2.0; [Co+Al] = 0.15 M; Urea = 10 × [Al]) was placed in a 50-mL Teflon® inner vessel within a stainless steel outer vessel (San'ai Kagaku). The mixture was allowed to react at 110 °C for 1 day under air-tight conditions. The resulting product was filtered, washed and vacuum-dried to yield CO_3^{2-}CoAl-LDH2 (145 mg) as pink powder.

Cl^{-}CoAl-LDH2 was prepared as follows: A mixed suspension of CO_3^{2-}CoAl-LDH2 (104 mg) in 50 mL of 0.1 M acetate-buffer/ NaCl mixed solution with AcOH ratio ([AcOH]/([AcOH]+[AcONa])) = 0.150 and with NaCl concentration = 2M. Under N_2 flow (500 $mL \cdot min^{-1}$), mixed suspension was stirred for 2 h at room temperature (~ 25 °C). The resulting product was filtered, washed with degassed deionized water and vacuum-dried to yield pink powder of Cl^{-}CoAl-LDH2 (99 mg).

S-3. FTIR spectra of MgAl-LDHs.

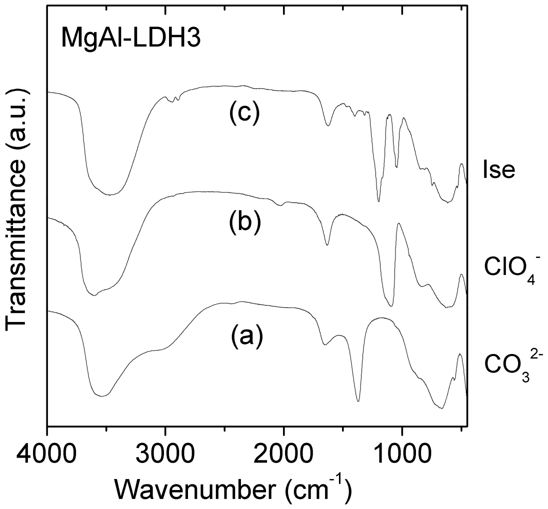


Fig. S-3-1. FTIR profiles of (a) initial CO_3^{2-}MgAl-LDH3, (b) ClO_4^-MgAl-LDH3, and (c) Ise-MgAl-LDH3. MgAl-LDH3 stands for the LDH composed of Mg and Al with Mg/Al mol ratio = 3 and Ise is for isethionate.

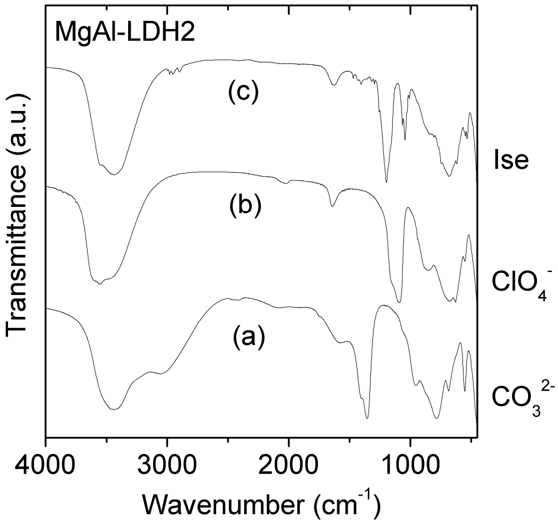
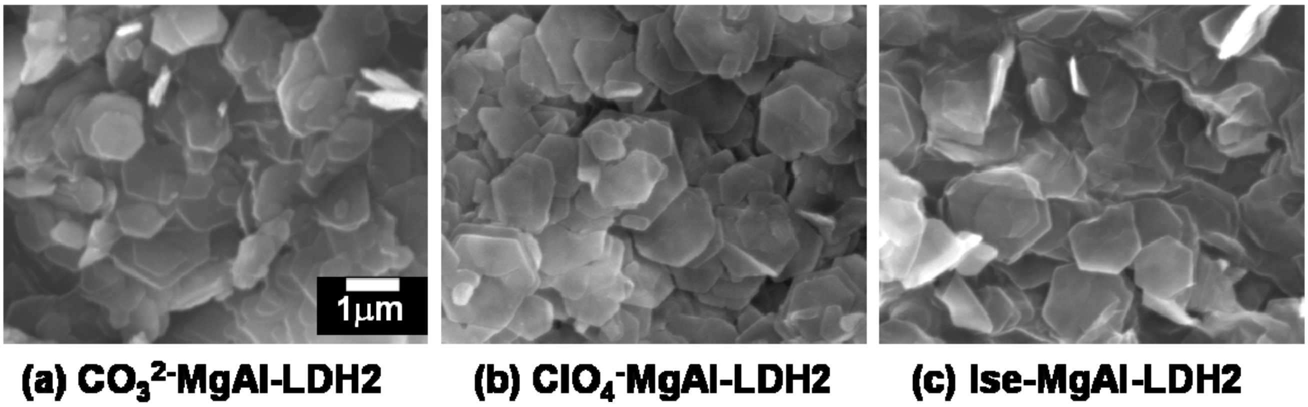


Fig. S-3-2. FTIR profiles of (a) initial CO_3^{2-}MgAl-LDH2, (b) ClO_4^-MgAl-LDH2, and (c) Ise-MgAl-LDH2.

S-4. SEM images of MgAl-LDH2s.



(a) CO_3^{2-}MgAl-LDH2 (b) ClO_4^-MgAl-LDH2 (c) Ise-MgAl-LDH2

Fig. S-4-1. SEM images of (a) the starting CO_3^{2-}MgAl-LDH2, (b) ClO_4^-MgAl-LDH2, and (c) Ise-MgAl-LDH2.

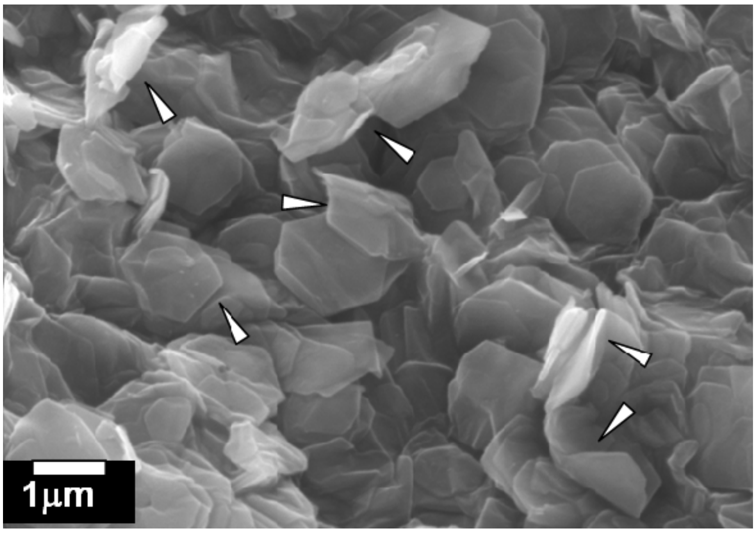


Fig. S-4-2. SEM photos of Ise-MgAl-LDH2 crystals which show bending and curling at the edges. It indicates the softness of the crystals**.**

S-5: Change in basal spacing with relative humidity (RH%) for Ise-MgAl-LDH3s.

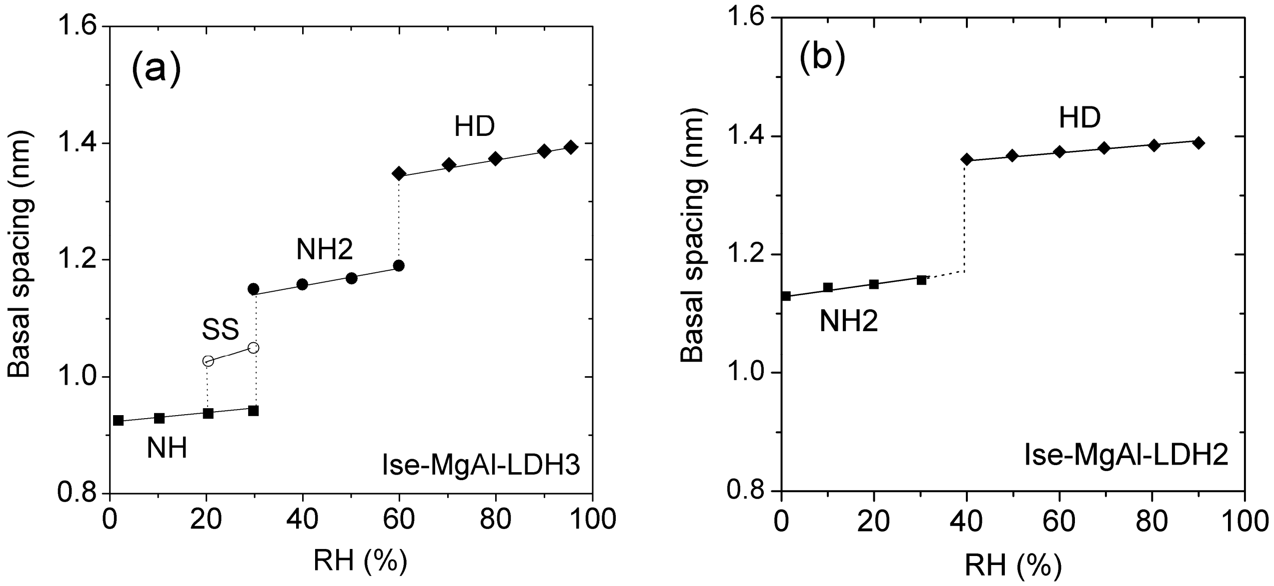


Fig. S-5. The change in basal spacing with relative humidity (RH%) for (a) Ise-MgAl-LDH3 and (b) Ise-MgAl-LDH2.

S-6. Powder XRD profile of Ise-MgAl-LDH3 at RH = 30%.

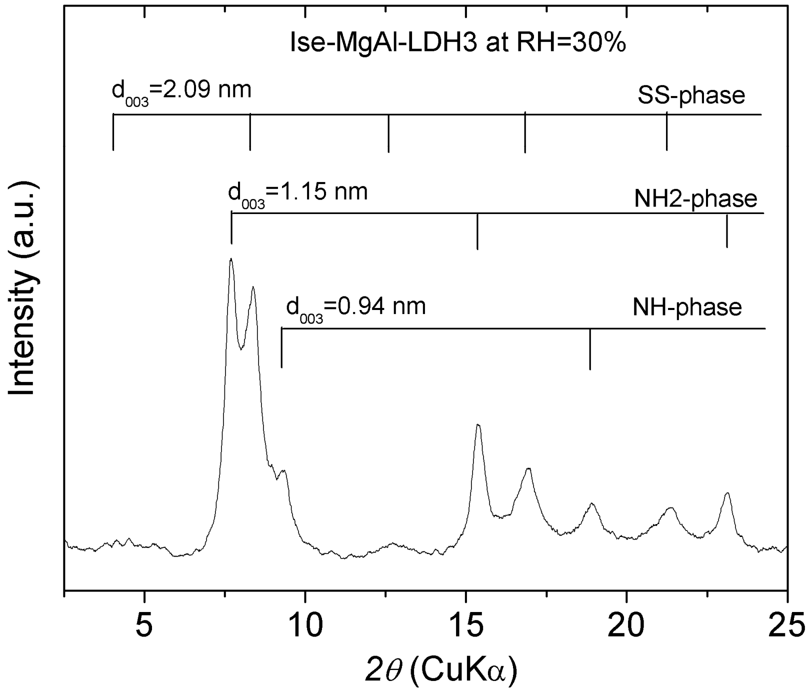
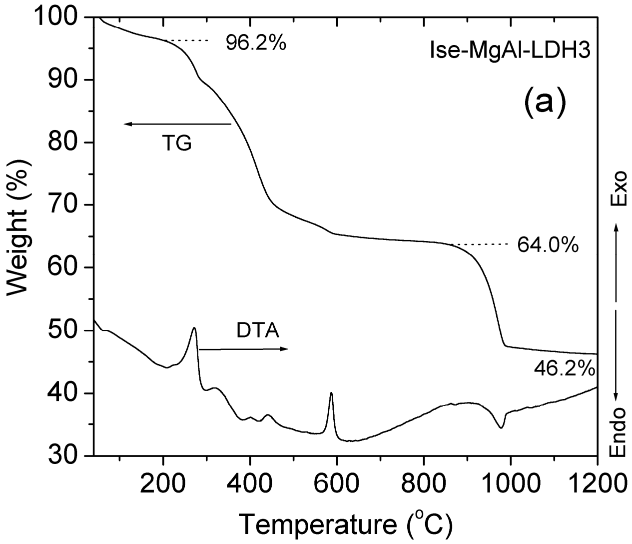


Fig. S-6. XRD profile of Ise-MgAl-LDH3 at RH = 30%. This profile is composed of the reflections attributable to the NH-, SS-, and NH2-phases.

S-7. TG/DTA diagrams for Ise-MgAl-LDHs.



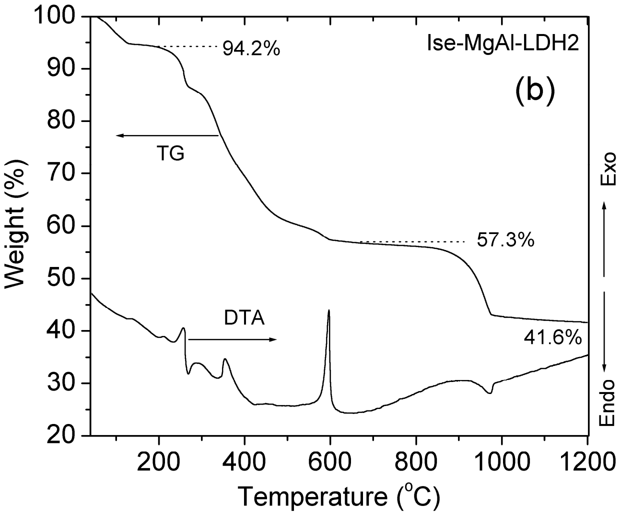


Fig. S-7. TG-DTA diagrams for (a) Ise-MgAl-LDH3, and (b) Ise-MgAl-LDH2. The specimen was dried under N_2 flow for 1h, and then, temperature was increased. The measurements were conducted under air flow.

S-8. TG-diagram for Ise-MgAl-LDH3 measured under air flow.

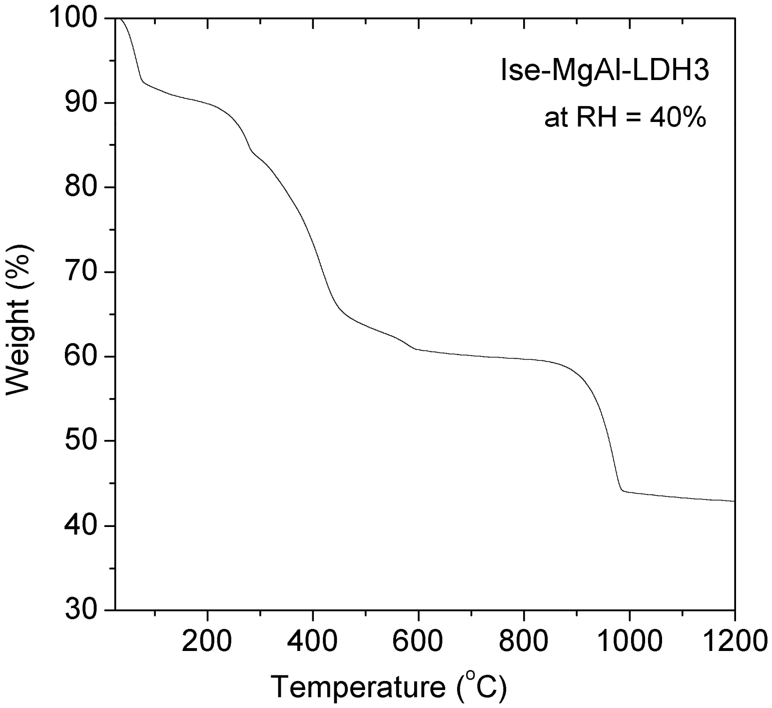


Fig. S-8. TG-diagram for Ise-MgAl-LDH3 measured under air flow. The specimen was not previously dried. The RH of air was 40%.

S-9. Change in powder XRD profile by the action of water.

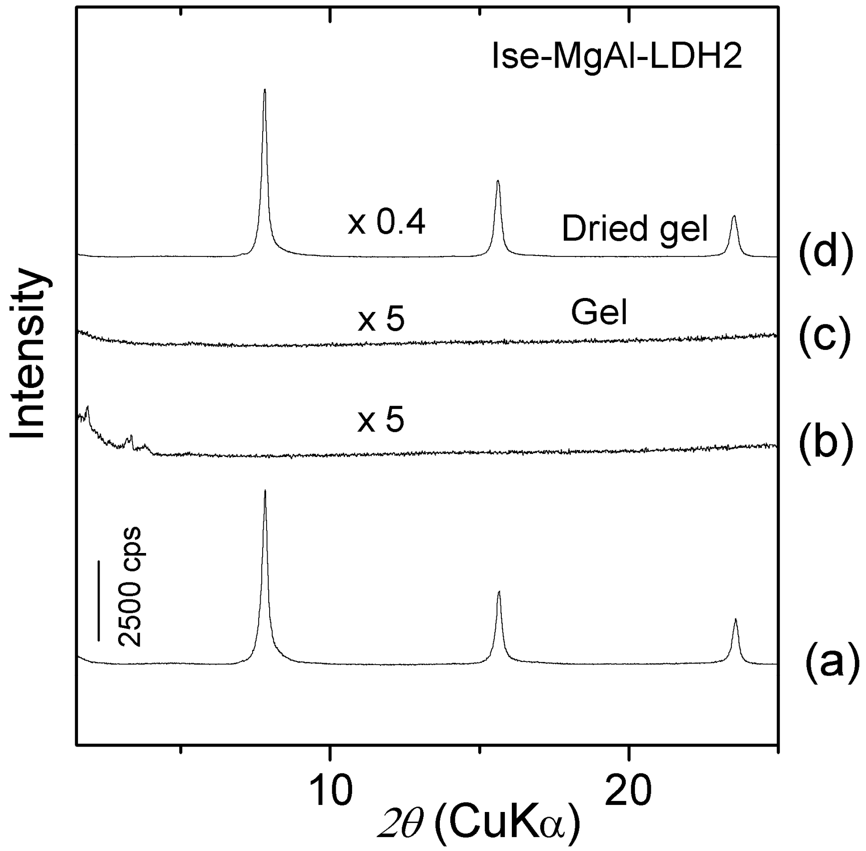


Fig. S-9. PXRD profiles of (a) Ise-MgAl-LDH2 powder spread on a glass plate, (b) the gel formed just after adding water to the powder, (c) the gel formed 20 min after adding water, and (d) the film obtained by drying the gel . The measurements were conducted under N_2 flow. The intensity was multiplied by the factor indicated for (b), (c) and (d).

S-10. AFM image of Ise-MgAl-LDH3 nanosheets

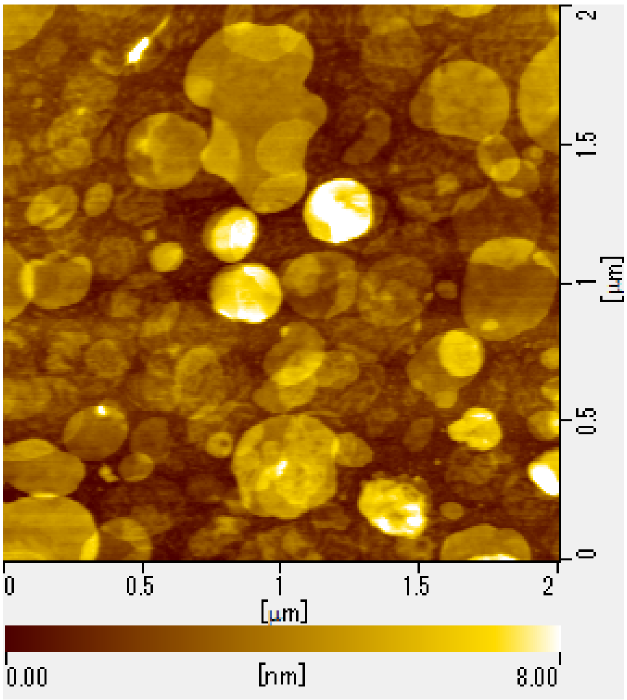


Fig. S-10. Tapping-mode AFM image of heavily stacked Ise-MgAl-LDH3 nanosheets on a Si wafer. The height is indicated by gray-scale display.

S-11. AFM images of Ise-MgAl-LDH2 nanosheet

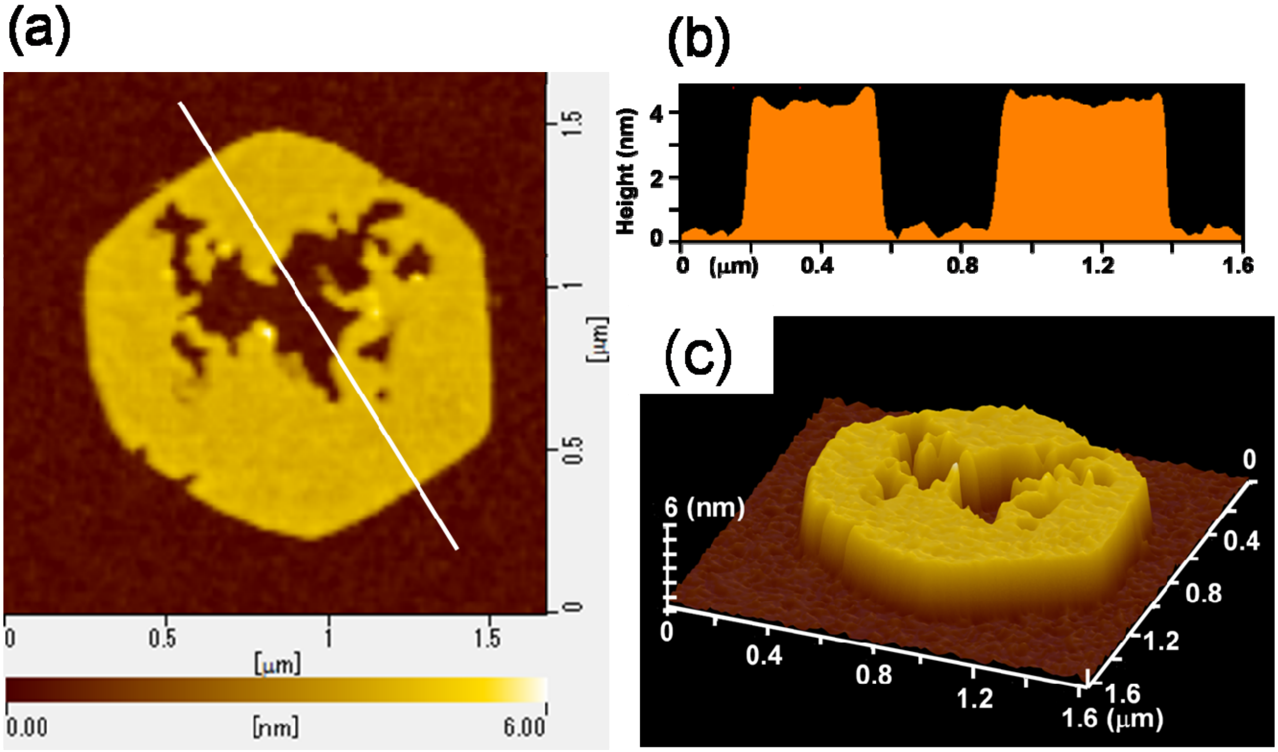


Fig. S-11. Tapping-mode AFM images of an Ise-MgAl-LDH2 nanosheet on a Si wafer precoated with PEI and PSS. (a) AFM image from above, and (b) height profile along the white line indicated in (a). The corresponding 3-D AFM image is in (c). The nanosheet retains the initial crystal shape (hexagonal), and size. The central part of the nanosheet is partly perforated due to its fragility.

S-12. FTIR profiles of NiAl-LDH3s.

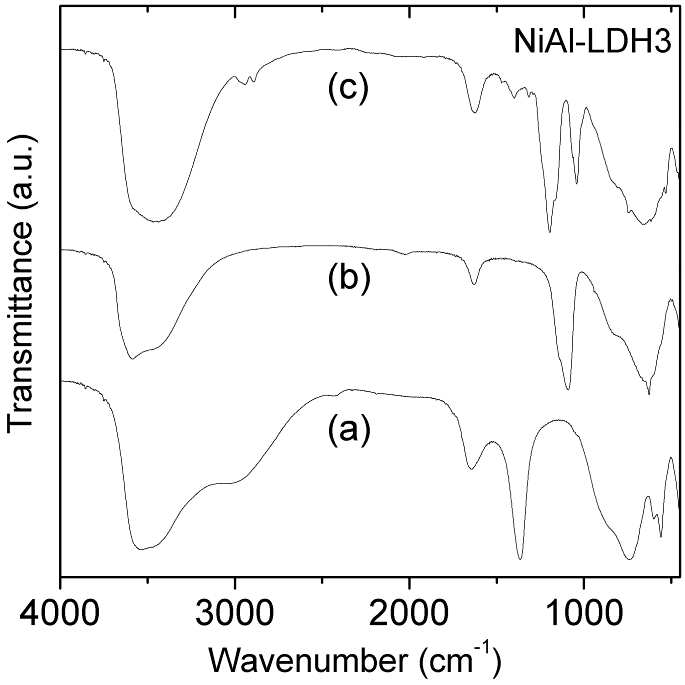


Fig. S-12. FTIR profiles of (a) initial CO_3^{2-}NiAl-LDH3, (b) ClO_4^-NiAl-LDH3, (c) Ise-NiAl-LDH3.

S-13. FTIR profiles of NiAl-LDH4s.

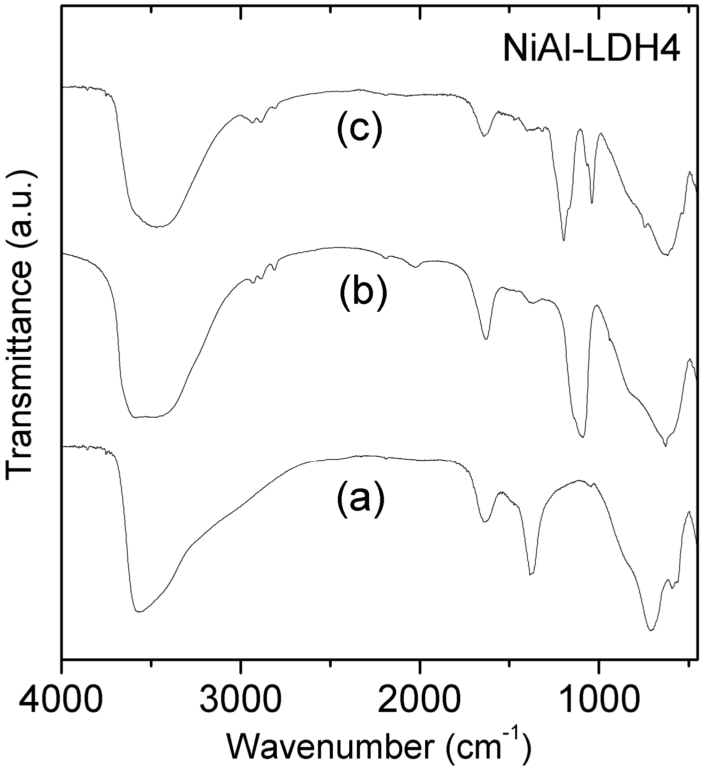


Fig. S-13. FTIR profiles of (a) initial CO_3^{2-}NiAl-LDH4, (b) ClO_4^-NiAl-LDH4, (c) Ise-NiAl-LDH4.

S-14. SEM images of NiAl-LDH2s.

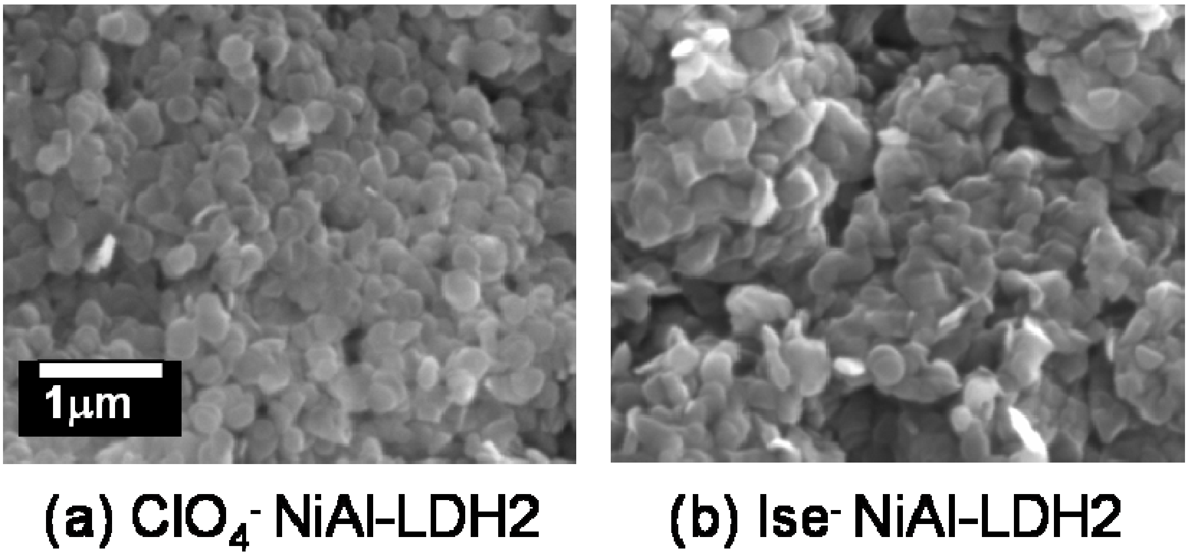


Fig. S-14. SEM images of (a) ClO_4^-NiAl-LDH2, and (b) Ise-NiAl-LDH2.

S-15. PXRD profiles of CoAl-LDH2s.

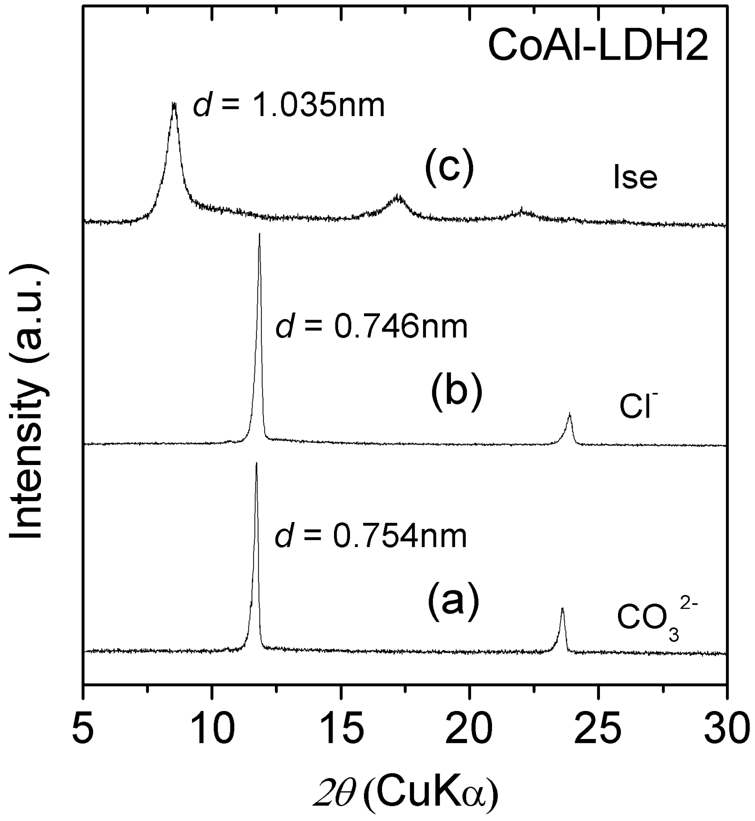
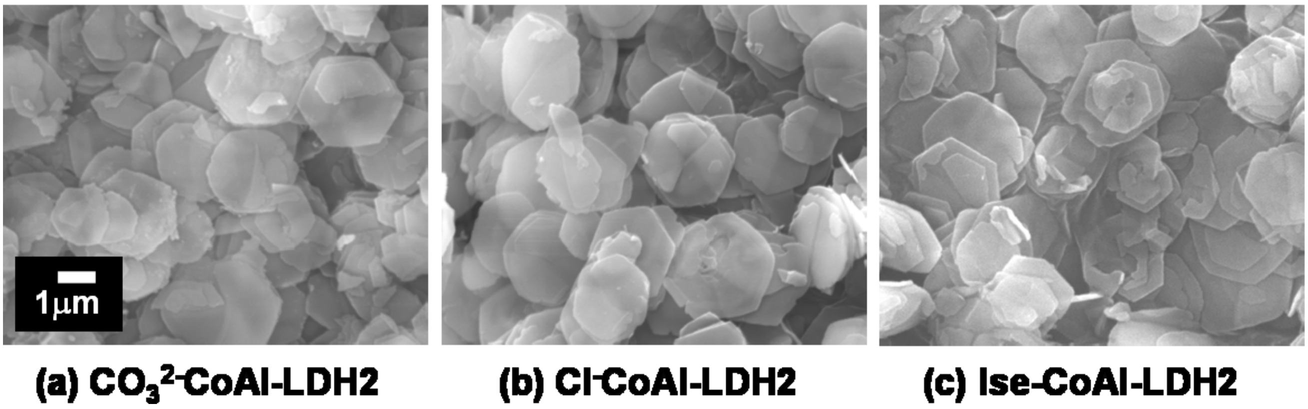


Fig. S-15. PXRD profiles of (a) the starting CO_3^{2-}CoAl-LDH2, (b) Cl^-CoAl-LDH2, and (c) Ise-CoAl-LDH2.

S-16. SEM images of CoAl-LDH2s.



(a) CO_3^{2-}CoAl-LDH2 (b) Cl^-CoAl-LDH2 (c) Ise-CoAl-LDH2

Fig. S-16. SEM images of (a) the starting CO_3^{2-}CoAl-LDH2, (b) Cl^-CoAl-LDH2, and (c) Ise-CoAl-LDH2.