Synthesis and Characterisation of Aqueous Miscible Organic-Layered Double Hydroxides

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1. Experimental details

1.1 The synthesis of Mg_2Al-CO_3-10 LDHs

The metal precursor solution (50 mL) of 0.75 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.375 M $Al(NO_3)_3 \cdot 9H_2O$ was added drop-wise into the 50 mL of 0.5 M Na_2CO_3 base solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Mg_2Al-CO_3-10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1-2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Mg_2Al-CO_3-10-A.

1.2 The synthesis of Mg_3Al-CO_3-12 LDHs

The metal precursor solution (50 mL) of 0.75 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.25 M $Al(NO_3)_3 \cdot 9H_2O$ was added drop-wise into the 50 mL of 0.5 M Na_2CO_3 base solution. The pH value was kept at *ca.* 12.0 by wise-dropping 4.0 M NaOH solution. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Mg_3Al-CO_3-12-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1-2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Mg_3Al-CO_3-12-A. When method was used as AMO solvent, the final sample name is Mg_3Al-CO_3-12-M.

1.3 The synthesis of Mg_3Al-NO_3-10 LDHs

The metal precursor solution (50 mL) of 0.75 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.25 M $Al(NO_3)_3 \cdot 9H_2O$ was added drop-wise into the 50 mL of 0.5 M $NaNO_3$ base solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During this synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Mg_3Al-NO_3-10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the

LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Mg_3Al-NO_3-10-A.

1.4 The synthesis of Mg_3Al-SO_4-10 LDHs

The metal precursor solution (50 mL) of 0.75 M $MgSO_4 \cdot 7H_2O$ and 0.25 M $Al_3(SO_4)_2 \cdot 16H_2O$ was added drop-wise into the 50 mL of 0.5 M Na_2SO_4 base solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During the synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Mg_3Al-SO_4-10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Mg_3Al-SO_4-10-A.

1.5 The synthesis of Mg_3Al-Cl-10 LDHs

The metal precursor solution (50 mL) of 0.75 M $MgCl_2 \cdot 6H_2O$ and 0.25 M $AlCl_3 \cdot 6H_2O$ was added drop-wise into the 50 mL of 0.5 M NaCl base solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During the synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Mg_3Al-Cl-10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Mg_3Al-Cl-10-A.

1.6 The synthesis of $Mg_3Al_{0.5}Fe_{0.5}$-NO_3 -10 LDHs

The metal precursor solution (50 mL) of 0.75 M $Mg(NO_3)_2 \cdot 6H_2O$, 0.125 M $Al(NO_3)_3 \cdot 9H_2O$ and 0.125 M $Fe(NO_3)_3 \cdot 9H_2O$ was added drop-wise into the 50 mL of 0.5 M $NaNO_3$ base solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During the synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as $Mg_3Al_{0.5}Fe_{0.5}$-NO_3 -10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as $Mg_3Al_{0.5}Fe_{0.5}$-NO_3 -10-A.

1.7 The synthesis of Zn_2Al-Borate-8.3 and Mg_3Al-Borate-9 LDHs

The synthesis of Zn_2Al-Borate-8.3 and Mg_3Al-Borate-9 was according to our previous report[1]. The metal precursor solution (50 mL) of 0.75 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.375 M $Al(NO_3)_3{\cdot}9H_2O$ was added drop-wise into the 50 mL of 1.87 M H_3BO_3 solution base solution. The pH value was kept at *ca.* 8.3 by wise-dropping 1.0 M NaOH solution. During the synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes 30 min. After aging for 16 h with stirring at 65 °C, the mixture was filtered and washed with DI water until the pH was close to 7. Then the product was dried in the vacuum oven overnight. The final sample was named as Zn_2Al-Borate-8.3-10-W. In the AMOST method, all the nucleation aging steps are the same as those in the conventional method. The LDH precursor was washed with DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named as Zn_2Al-Borate-8.3-A.

Similarly, Mg_3Al-borate LDH was synthesized at pH 9 using 50 mL of 0.75 M $Mg(NO_3)_2{\cdot}6H_2O$ and 0.25 M $Al(NO_3)_3{\cdot}9H_2O$ solution drop-wise into a 50 mL of 1.87 M H_3BO_3 solution. During the synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric CO_2. This nucleation process usually takes us 30 min. After aging for 16 h with stirring at 65 °C, the mixture was filtered and washed with DI water until the pH was close to 7. Then the mixture was dried in the vacuum oven overnight. The final sample was named as Mg_3Al-Borate-9-W.All the previous steps are the same with the conventional method except the water washed LDHs wet cake was re-dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h several times. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room temperature for overnight. The sample was named Mg_3Al-Borate-9-A.

2. Characterization

2.1 X-ray diffraction

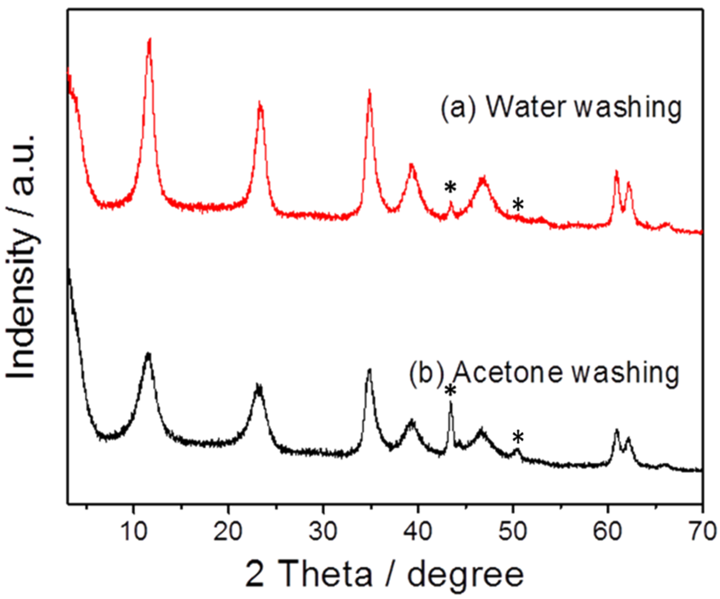

Fig. S1 XRD patterns of $Mg_2Al\text{-}CO_3$-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent. (*) are Bragg reflections from the Al sample holder.

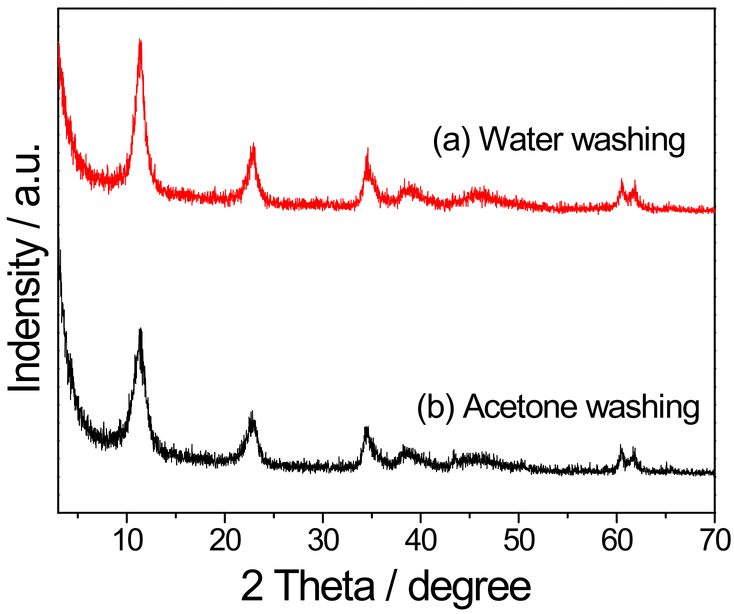

Fig. S2 XRD patterns of $Mg_3Al\text{-}CO_3$-12 (a) sample prepared by conventional co-precipitation method in water at pH 12 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

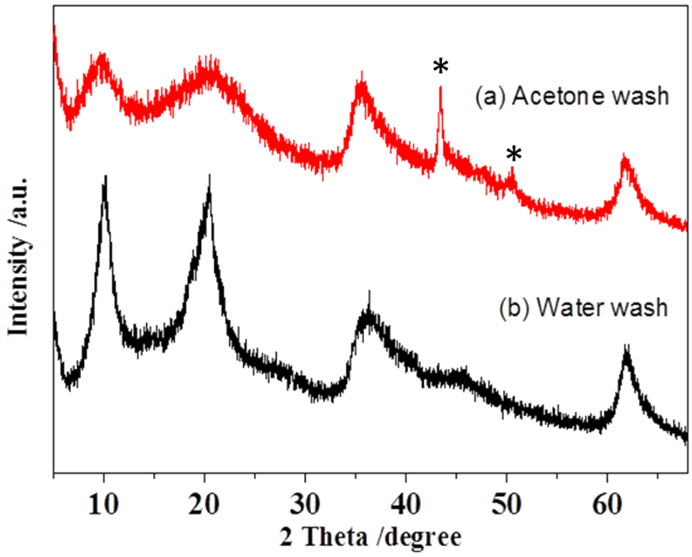

Fig. S3 XRD patterns of Mg_3Al-SO_4-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent. (*) are Bragg reflections from the Al sample holder.

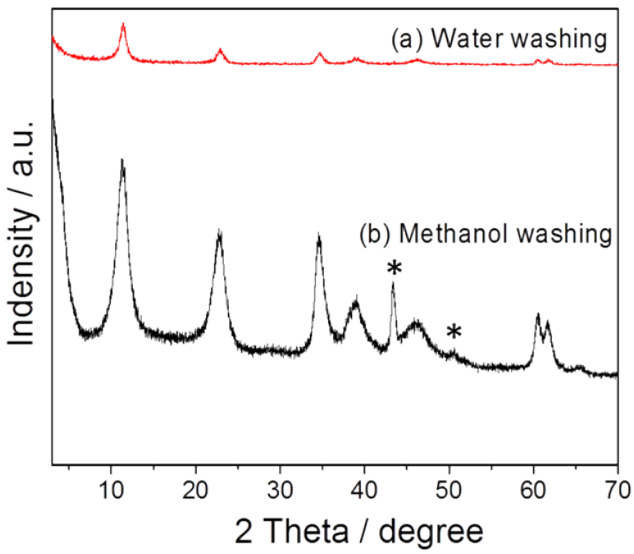

Fig. S4 XRD patterns of Mg_3Al-CO_3-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent. (*) are Bragg reflections from the Al sample holder

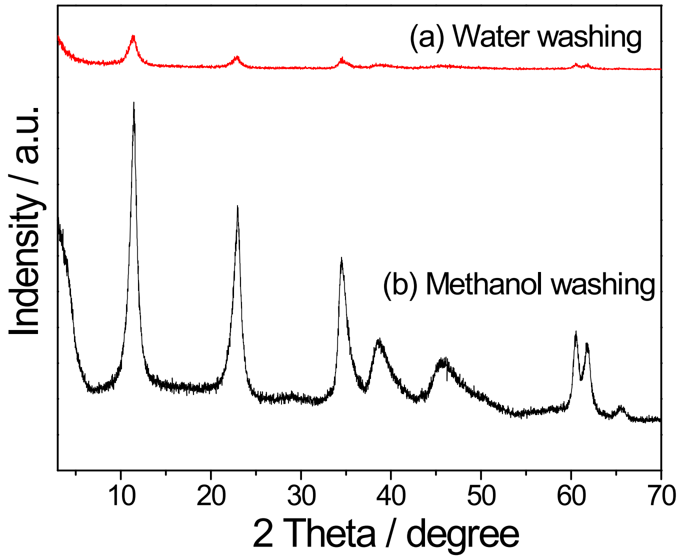

Fig. S5 XRD patterns of Mg_3Al-SO_4-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent.

2.2 Infrared spectroscopy

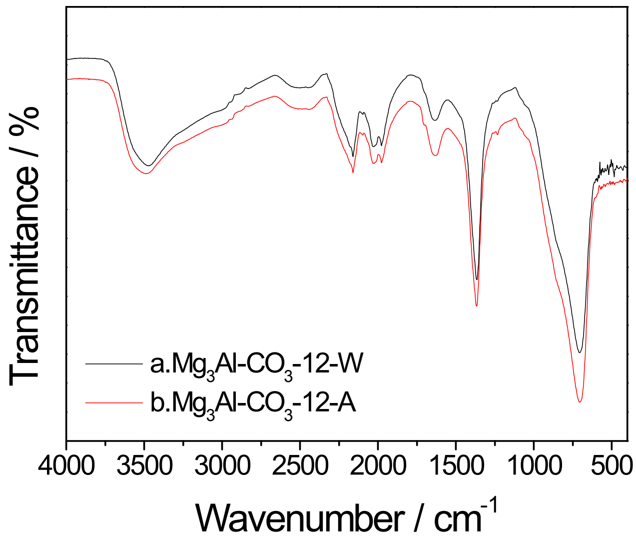

Fig. S6 FTIR patterns of Mg_3Al-CO_3-12 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

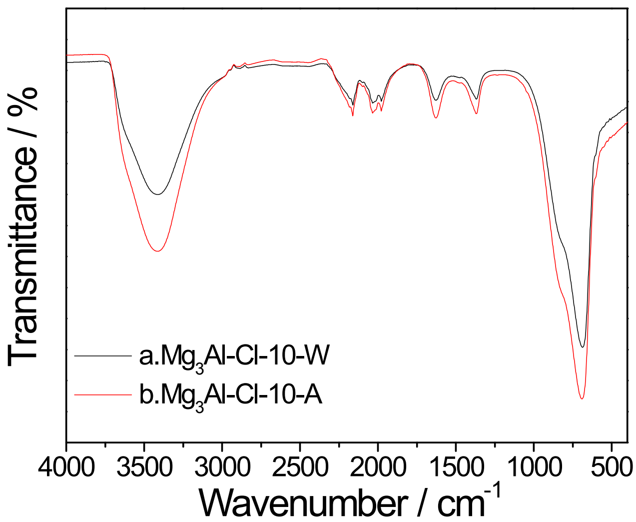

Fig. S7 FTIR patterns of Mg_3Al-Cl-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

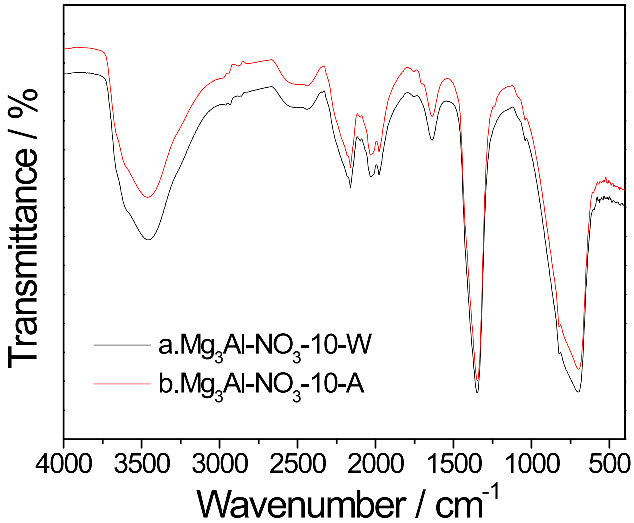

Fig. S8 FTIR patterns of Mg_3Al-NO_3-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

2.3 Transmission Electron Microscopy

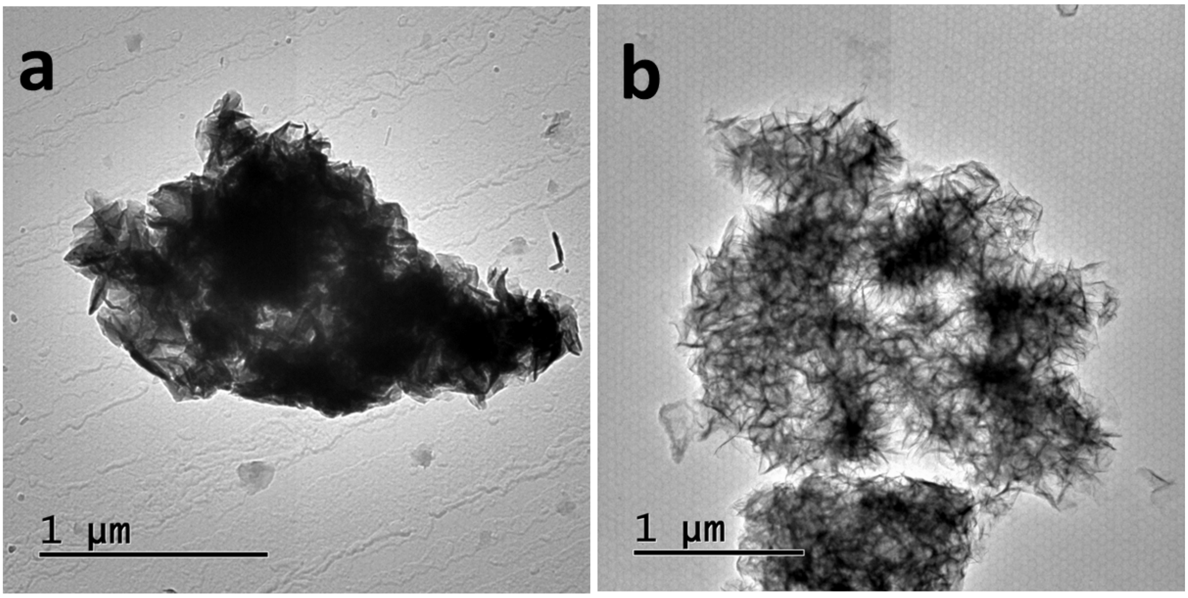

Fig. S9 TEM patterns of Mg_3Al-Cl-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

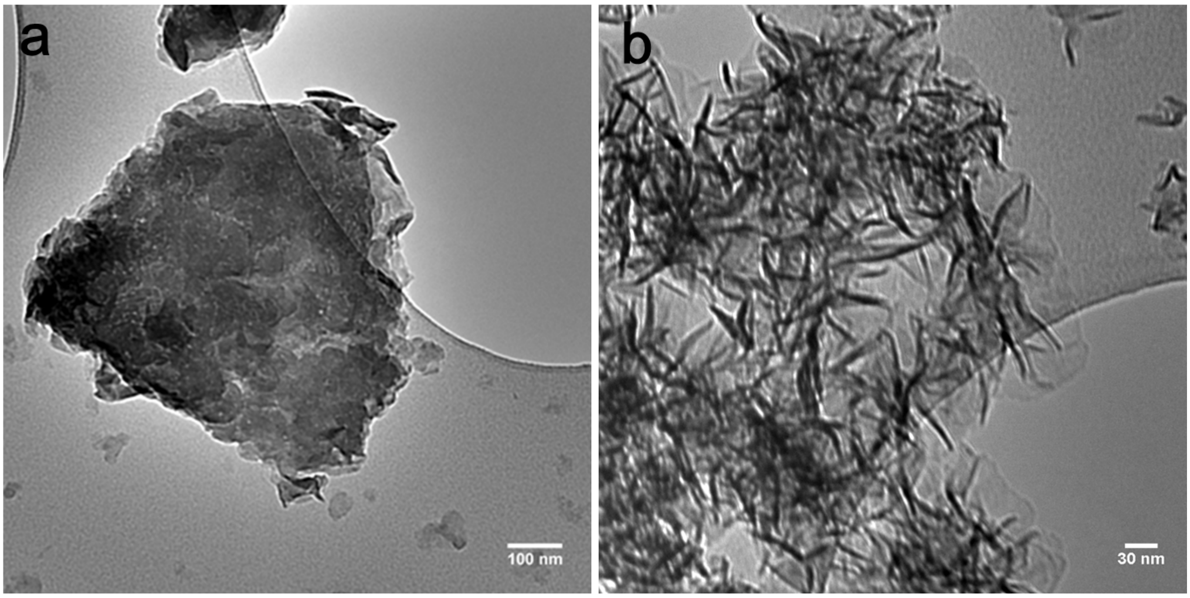

Fig. S10 TEM patterns of $Mg_3Al\text{-}NO_3$-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

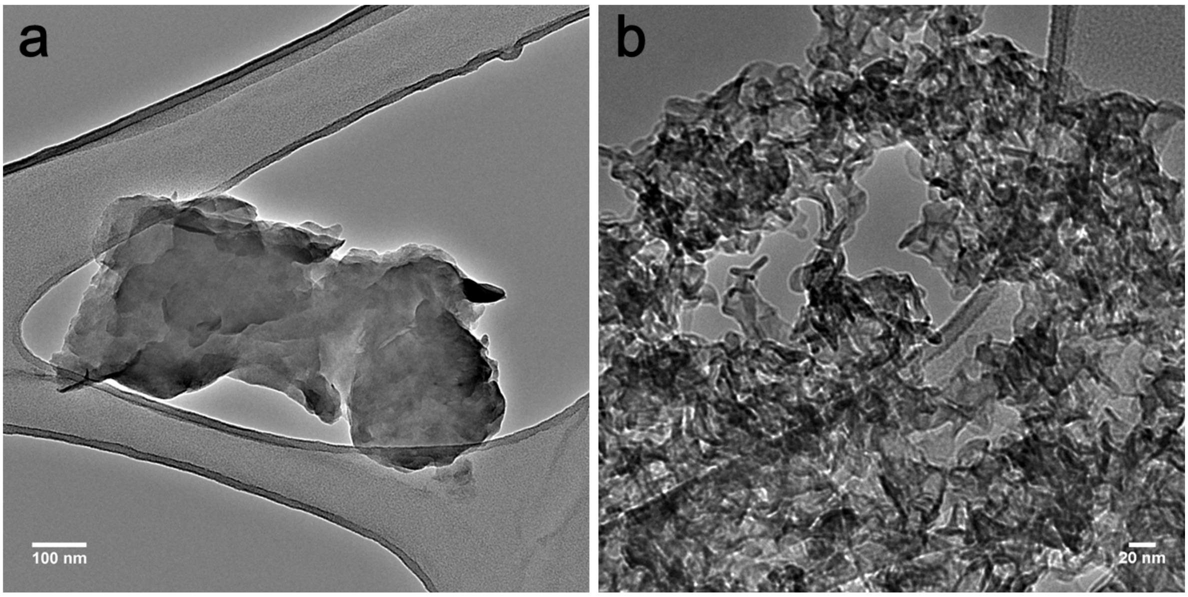

Fig. S11 TEM patterns of $Mg_3Al\text{-}SO_4$-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

2.4 Scanning Electron Microscopy

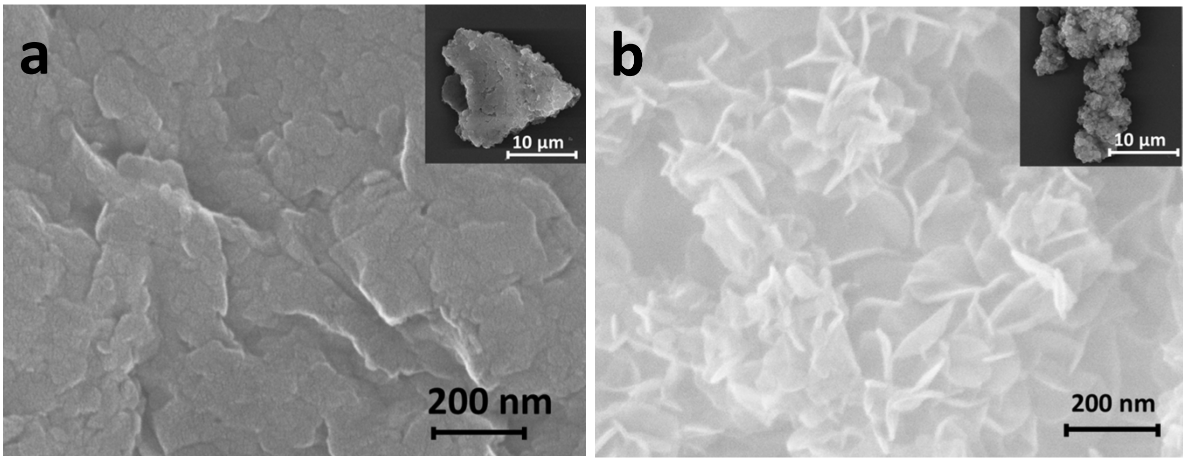

Fig. S12 TEM patterns of Mg_3Al-Cl-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

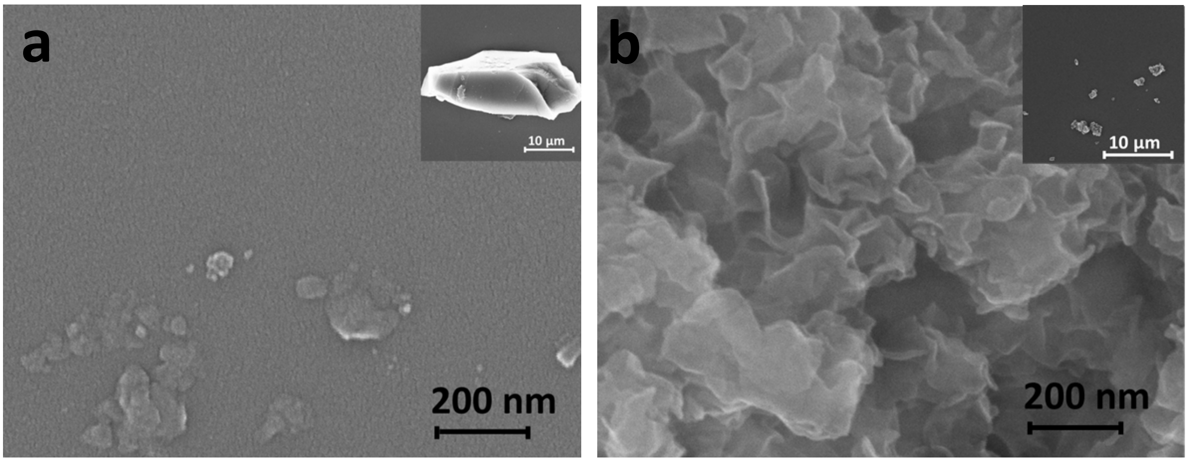

Fig. S13 TEM patterns of Mg_3Al-NO_3-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

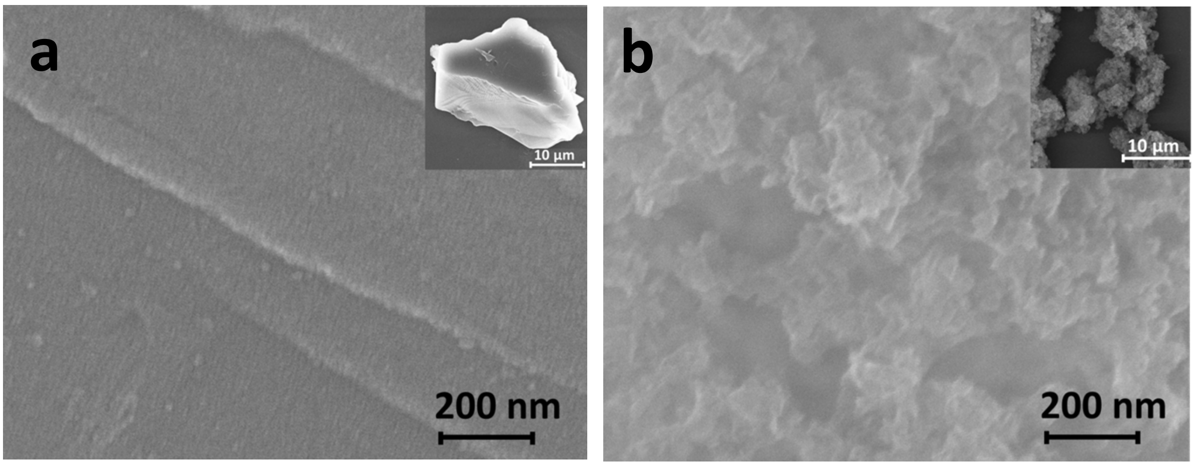

Fig. S14 TEM patterns of Mg_3Al-SO_4-10 (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

2.5 Thermogravimetric analysis

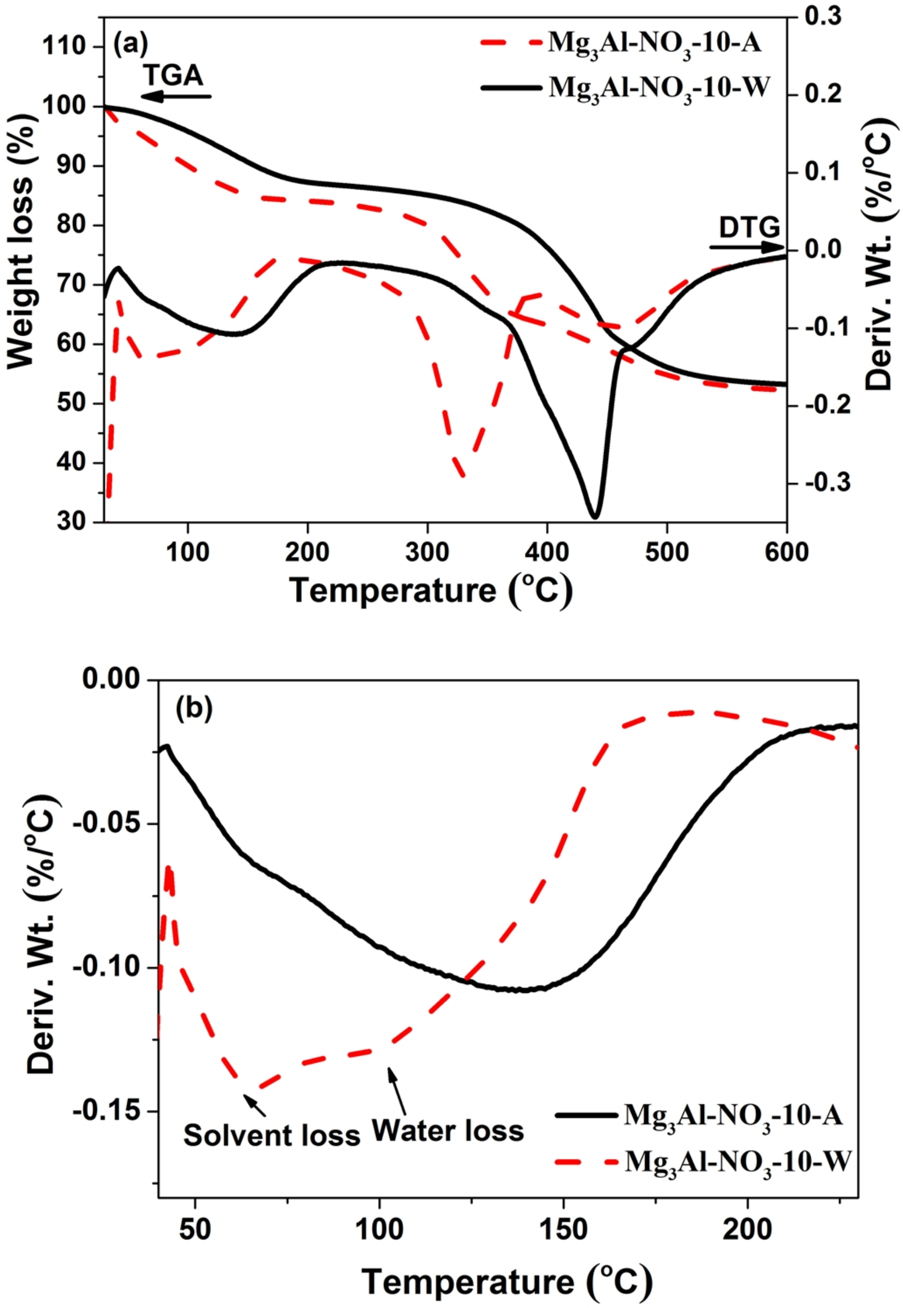

Fig. S15. TGA and DTG analysis of $Mg_3Al\text{-}NO_3$-10 LDHs (a) in the range of 30-600 °C; (b) in the range of 30-230 °C; $Mg_3Al\text{-}NO_3$-10-W prepared by a conventional co-precipitation method in water at pH 10. $Mg_3Al\text{-}NO_3$-10-A is prepared by identical conditions in water at pH 10 according to the AMOST method using acetone as the AMO-solvent.

Table S1 Summary of water and AMO-solvent content in the AMO-LDHs compared to conventional C-LDHs as determined by analysis of the TGA data.

LDH	C-LDH[2]		AMO-LDH-A[1]		AMO-LDH-M[1]	
	b[3]	*c*[4]	*b*[3]	*c*[4]	*b*[3]	*c*[4]
Mg_3Al-CO_3-10	0.41	0	0.34	0.04	--	--
Mg_3Al-CO_3-12	0.7	0	0.43	0.11	0.44	0.11
Mg_2Al-CO_3-10	1.05	0	0.59	0.18	--	--
Mg_3Al-Cl-10	0.58	0	0.46	0.04	--	--
Mg_3Al-SO_4-10	0.77	0	0.71	0.17	--	--
Mg_3Al-NO_3-10	0.57	0	0.38	0.12	--	--
$Mg_3Al_{0.5}Fe_{0.5}$-10	0.74	0	0.5	0.06	--	--

[1]AMO-LDH-A and AMO-LDH-M are the LDH with the formula of $[M^{z+}_{1-x}M'^{y+}_{x}(OH)_2]^{a+}(X^{n-})_{a/r}{\bullet}bH_2O{\bullet}c$(AMO-solvent) (**1**); wherein M and M' are metal cations, z = 1 or 2; y = 3 or 4, 0< x <1, b =0-10, c = 0-10, X is an anion, r = 1 to 3 and $a = z(1-x)+xy-2$. AMO-solvent (A = Acetone, M = Methanol).

[2]C-LDH is an LDH with the formula $[M^{z+}_{1-x}M'^{y+}_{x}(OH)_2]^{a+}(X^{n-})_{a/r}{\bullet}bH_2O$ (**2**) ; wherein M and M' are metal cations, z = 1 or 2; y = 3 or 4, 0<x<1, b =0-10, c = 0-10, X is an anion, r = 1 to 3 and $a = z(1-x)+xy-2$.

[3]*b* is the water content in the formula (**1**) and (**2**).

[4]*c* is the acetone content in the formula (**1**).

2.6 BET Analysis

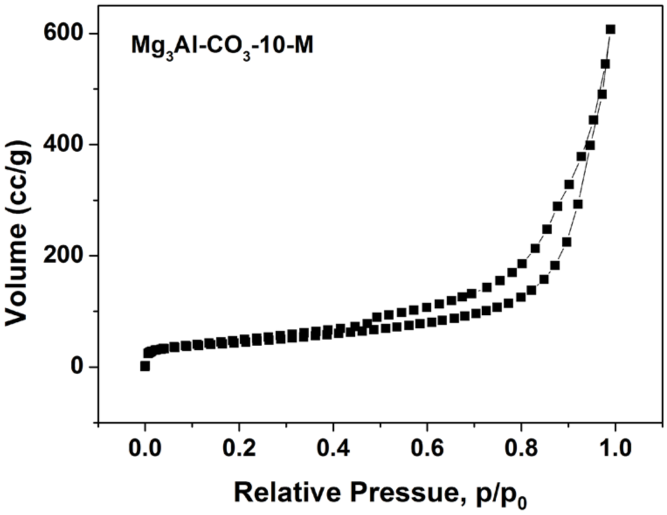

Fig. S16 BET Isotherms of Mg_3Al-CO_3-10 BET sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent.

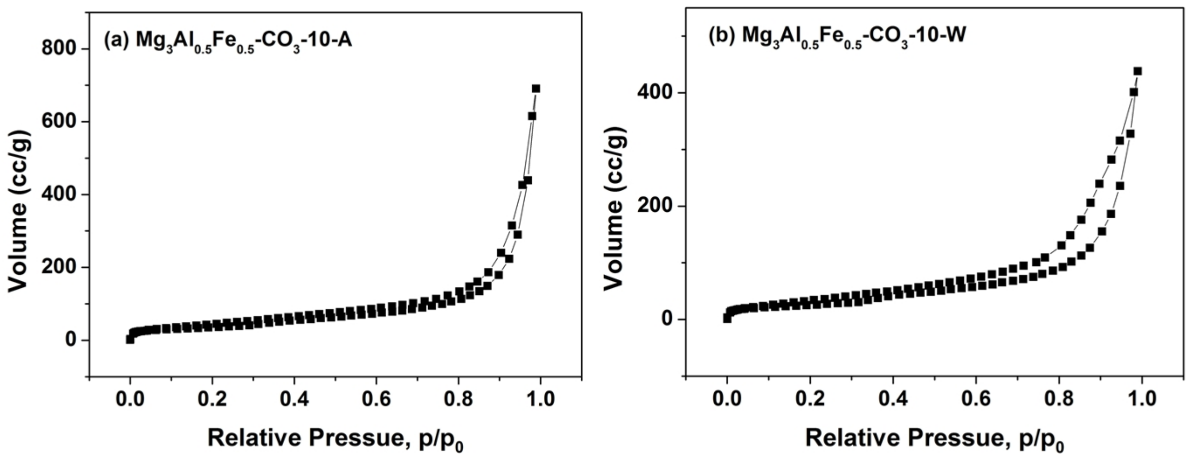

Fig. S17 BET Isotherms of $Mg_3Al_{0.5}Fe_{0.5}-CO_3$-10 (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent 10 (b) sample prepared by conventional co-precipitation method in water at pH.

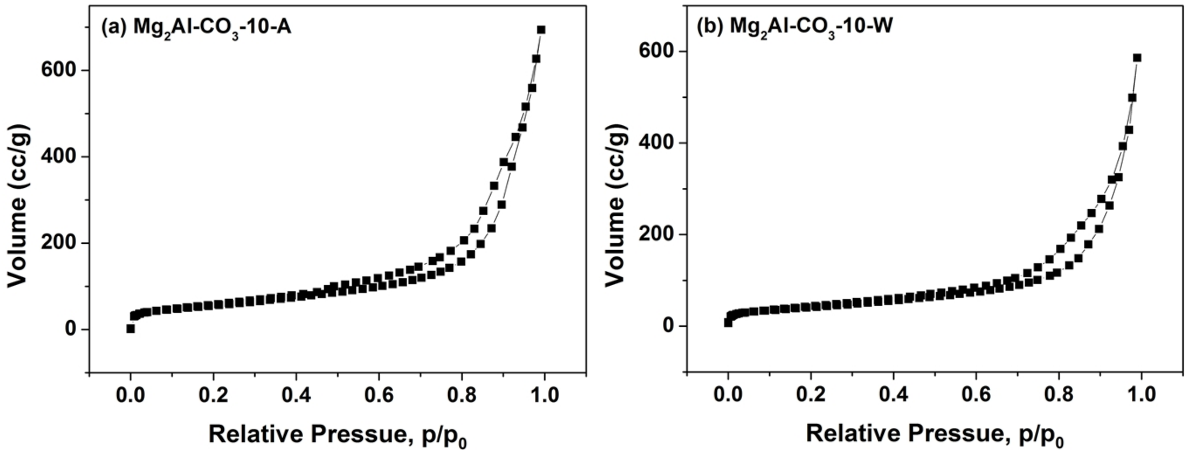

Fig. S18 BET Isotherms of Mg_2Al-CO_3-10 (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent (b) sample prepared by conventional co-precipitation method in water at pH 10.

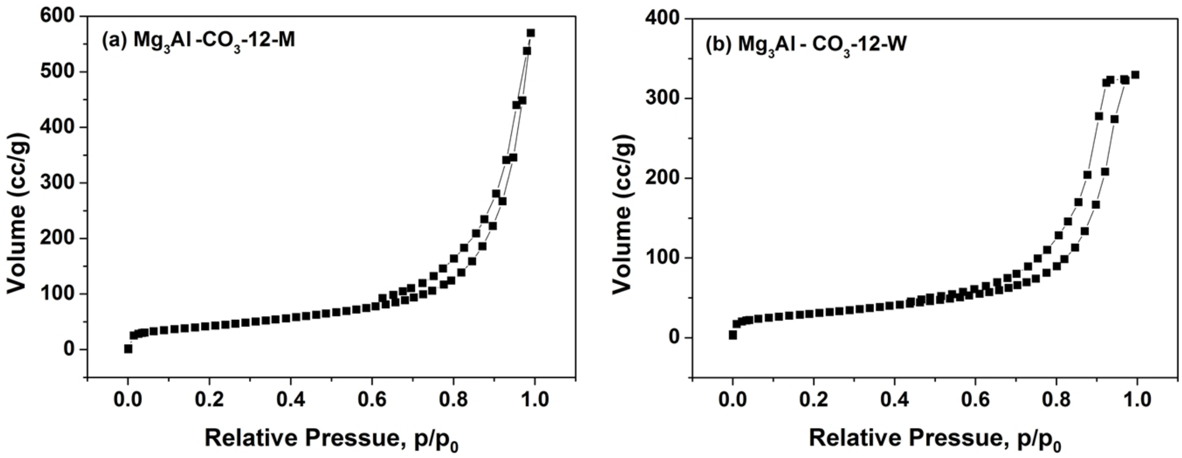

Fig. S19 BET Isotherms of Mg_3Al-CO_3-12 (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent (b) sample prepared by conventional co-precipitation method in water at pH 12.

2.7 Density studies

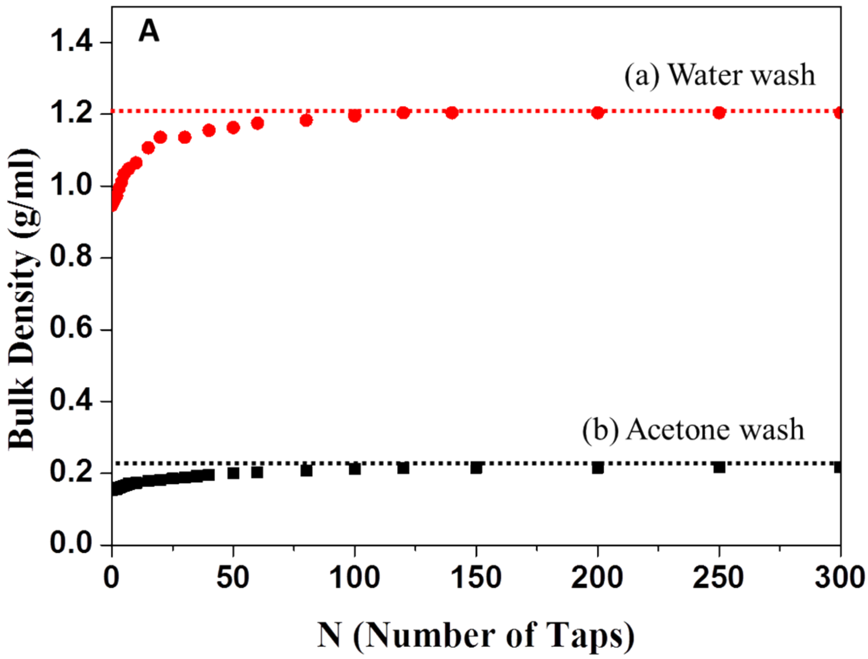

Fig. S20 Bulk density of Mg_3Al-NO_3-10 LDH; (a) sample prepared by a conventional co-precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent acetone.

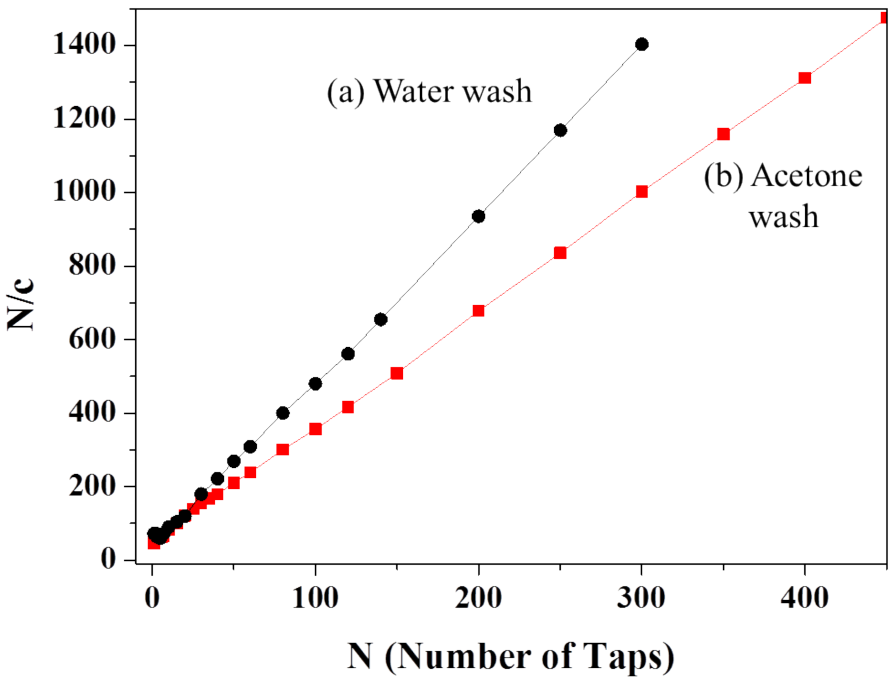

Fig. S21 Carr's index curves of Mg_3Al-NO_3-10 LDH; (a) sample prepared by a conventional co-precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent acetone.

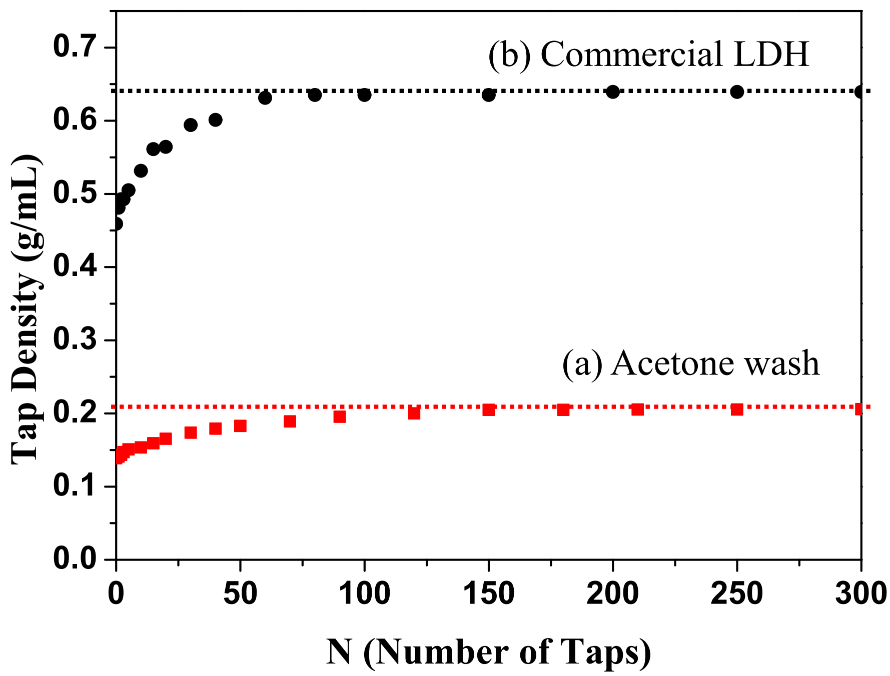

Fig. S22 Bulk density of Mg_3Al-CO_3-10 LDH; (a) sample prepared by a conventional co-precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent acetone.

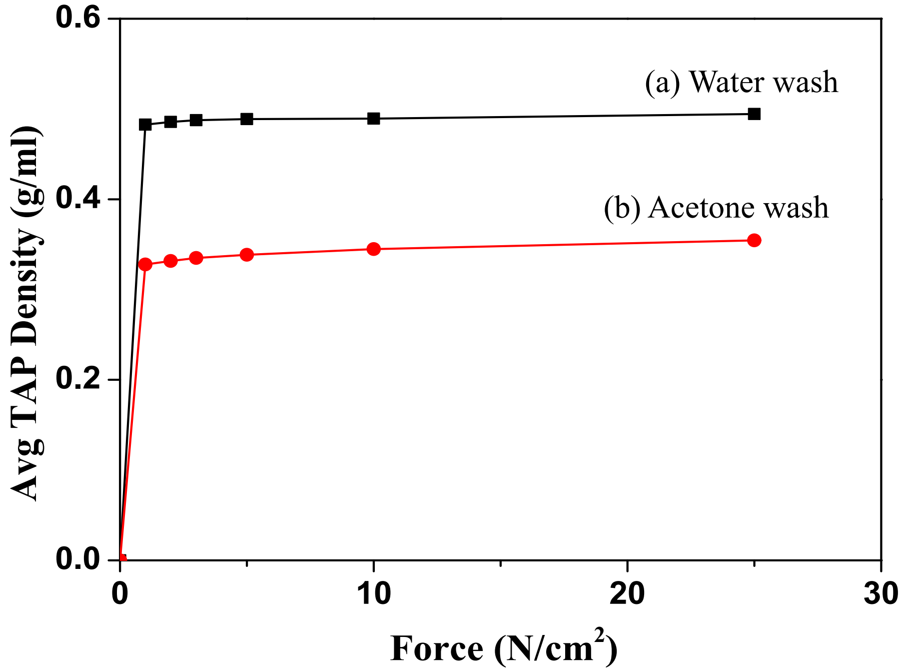

Fig. S23 GeoPyc T.A.P density of Mg_3Al-CO_3-10 LDH; (a) sample prepared by a conventional co-precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent acetone.

[1] Q. Wang and D. O'Hare, *Chemical Communications* 2013, **49**, 6301-6303.