

Synthesis and Characterisation of Aqueous Miscible Organic-Layered Double Hydroxides

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1. Experimental details

1.1 The synthesis of $\text{Mg}_2\text{Al-CO}_3\text{-10}$ LDHs

The metal precursor solution (50 mL) of 0.75 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.375 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Mg}_2\text{Al-CO}_3\text{-10-W}$. 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 $\text{Mg}_2\text{Al-CO}_3\text{-10-A}$.

1.2 The synthesis of $\text{Mg}_3\text{Al-CO}_3\text{-12}$ LDHs

The metal precursor solution (50 mL) of 0.75 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Mg}_3\text{Al-CO}_3\text{-12-W}$. 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 $\text{Mg}_3\text{Al-CO}_3\text{-12-A}$. When method was used as AMO solvent, the final sample name is $\text{Mg}_3\text{Al-CO}_3\text{-12-M}$.

1.3 The synthesis of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ LDHs

The metal precursor solution (50 mL) of 0.75 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Mg}_3\text{Al-NO}_3\text{-10-W}$. 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

1 LDH was filtered and washed thoroughly with acetone again. Finally, the product was dried
2 in the vacuum oven at room temperature for overnight. The sample was named as $\text{Mg}_3\text{Al-NO}_3\text{-10-A}$.

4 1.4 The synthesis of $\text{Mg}_3\text{Al-SO}_4\text{-10}$ LDHs

5 The metal precursor solution (50 mL) of 0.75 M $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.25 M $\text{Al}_3(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$
6 was added drop-wise into the 50 mL of 0.5 M Na_2SO_4 base solution. The pH value was kept
7 at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During the synthesis, the system was
8 purged with N_2 gas to prevent the contamination by atmospheric CO_2 . This nucleation
9 process usually takes 30 min. After aging for 16 h with stirring at room temperature, the
10 mixture was filtered and washed with DI water until the pH was close to 7. Then the product
11 was dried in the vacuum oven overnight. The final sample was named as $\text{Mg}_3\text{Al-SO}_4\text{-10-W}$.
12 In the AMOST method, all the nucleation aging steps are the same as those in the
13 conventional method. The LDH precursor was washed with DI water until the pH was close
14 to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake was
15 dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH was
16 filtered and washed thoroughly with acetone again. Finally, the product was dried in the
17 vacuum oven at room temperature for overnight. The sample was named as $\text{Mg}_3\text{Al-SO}_4\text{-10-A}$.

18 1.5 The synthesis of $\text{Mg}_3\text{Al-Cl-10}$ LDHs

19 The metal precursor solution (50 mL) of 0.75 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was
20 added drop-wise into the 50 mL of 0.5 M NaCl base solution. The pH value was kept at *ca.*
21 10.0 by wise-dropping 4.0 M NaOH solution. During the synthesis, the system was purged
22 with N_2 gas to prevent the contamination by atmospheric CO_2 . This nucleation process
23 usually takes 30 min. After aging for 16 h with stirring at room temperature, the mixture was
24 filtered and washed with DI water until the pH was close to 7. Then the product was dried in
25 the vacuum oven overnight. The final sample was named as $\text{Mg}_3\text{Al-Cl-10-W}$. In the AMOST
26 method, all the nucleation aging steps are the same as those in the conventional method. The
27 LDH precursor was washed with DI water until the pH was close to 7 following by being
28 rinsed with acetone thoroughly. The obtained LDH wet cake was dispersed in 200 mL
29 acetone and stirred at room temperature for 1 - 2 h. Then the LDH was filtered and washed
30 thoroughly with acetone again. Finally, the product was dried in the vacuum oven at room
31 temperature for overnight. The sample was named as $\text{Mg}_3\text{Al-Cl-10-A}$.

32 1.6 The synthesis of $\text{Mg}_3\text{Al}_{0.5}\text{Fe}_{0.5}\text{-NO}_3\text{-10}$ LDHs

33 The metal precursor solution (50 mL) of 0.75 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.125 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
34 and 0.125 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added drop-wise into the 50 mL of 0.5 M NaNO_3 base
35 solution. The pH value was kept at *ca.* 10.0 by wise-dropping 4.0 M NaOH solution. During
36 the synthesis, the system was purged with N_2 gas to prevent the contamination by
37 atmospheric CO_2 . This nucleation process usually takes 30 min. After aging for 16 h with
38 stirring at room temperature, the mixture was filtered and washed with DI water until the pH
39 was close to 7. Then the product was dried in the vacuum oven overnight. The final sample
40 was named as $\text{Mg}_3\text{Al}_{0.5}\text{Fe}_{0.5}\text{-NO}_3\text{-10-W}$. In the AMOST method, all the nucleation aging

1 steps are the same as those in the conventional method. The LDH precursor was washed with
2 DI water until the pH was close to 7 following by being rinsed with acetone thoroughly. The
3 obtained LDH wet cake was dispersed in 200 mL acetone and stirred at room temperature for
4 1 - 2 h. Then the LDH was filtered and washed thoroughly with acetone again. Finally, the
5 product was dried in the vacuum oven at room temperature for overnight. The sample was
6 named as $\text{Mg}_3\text{Al}_{0.5}\text{Fe}_{0.5}\text{-NO}_3$ -10-A.

7 1.7 The synthesis of Zn_2Al -Borate-8.3 and Mg_3Al -Borate-9 LDHs

8 The synthesis of Zn_2Al -Borate-8.3 and Mg_3Al -Borate-9 was according to our previous
9 report^[1]. The metal precursor solution (50 mL) of 0.75 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.375 M
10 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added drop-wise into the 50 mL of 1.87 M H_3BO_3 solution base solution.
11 The pH value was kept at *ca.* 8.3 by wise-dropping 1.0 M NaOH solution. During the
12 synthesis, the system was purged with N_2 gas to prevent the contamination by atmospheric
13 CO_2 . This nucleation process usually takes 30 min. After aging for 16 h with stirring at 65 °C,
14 the mixture was filtered and washed with DI water until the pH was close to 7. Then the
15 product was dried in the vacuum oven overnight. The final sample was named as Zn_2Al -
16 Borate-8.3-10-W. In the AMOST method, all the nucleation aging steps are the same as those
17 in the conventional method. The LDH precursor was washed with DI water until the pH was
18 close to 7 following by being rinsed with acetone thoroughly. The obtained LDH wet cake
19 was dispersed in 200 mL acetone and stirred at room temperature for 1 - 2 h. Then the LDH
20 was filtered and washed thoroughly with acetone again. Finally, the product was dried in the
21 vacuum oven at room temperature for overnight. The sample was named as Zn_2Al -Borate-
22 8.3-A.

23 Similarly, Mg_3Al -borate LDH was synthesized at pH 9 using 50 mL of 0.75 M
24 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution drop-wise into a 50 mL of 1.87 M
25 H_3BO_3 solution. During the synthesis, the system was purged with N_2 gas to prevent the
26 contamination by atmospheric CO_2 . This nucleation process usually takes us 30 min. After
27 aging for 16 h with stirring at 65 °C, the mixture was filtered and washed with DI water until
28 the pH was close to 7. Then the mixture was dried in the vacuum oven overnight. The final
29 sample was named as Mg_3Al -Borate-9-W. All the previous steps are the same with the
30 conventional method except the water washed LDHs wet cake was re-dispersed in 200 mL
31 acetone and stirred at room temperature for 1 - 2 h several times. Then the LDH was filtered
32 and washed thoroughly with acetone again. Finally, the product was dried in the vacuum
33 oven at room temperature for overnight. The sample was named Mg_3Al -Borate-9-A.

34 2. Characterization

35 2.1 X-ray diffraction

36

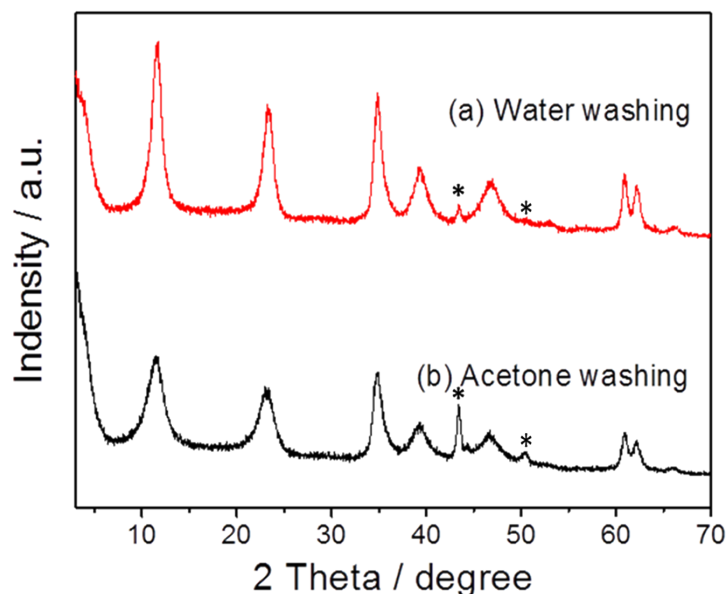


Fig. S1 XRD patterns of $\text{Mg}_2\text{Al-CO}_3\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent. (*) are Bragg reflections from the Al sample holder.

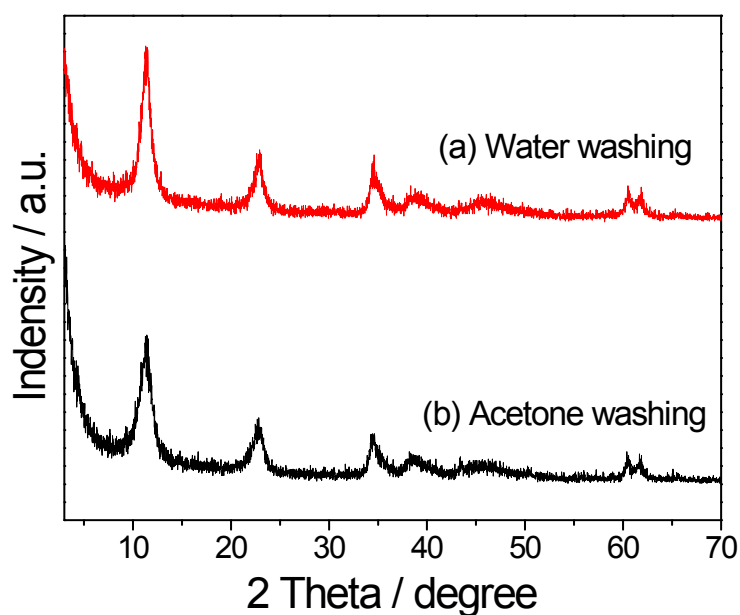


Fig. S2 XRD patterns of $\text{Mg}_3\text{Al-CO}_3\text{-12}$ (a) sample prepared by conventional co-precipitation method in water at pH 12 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

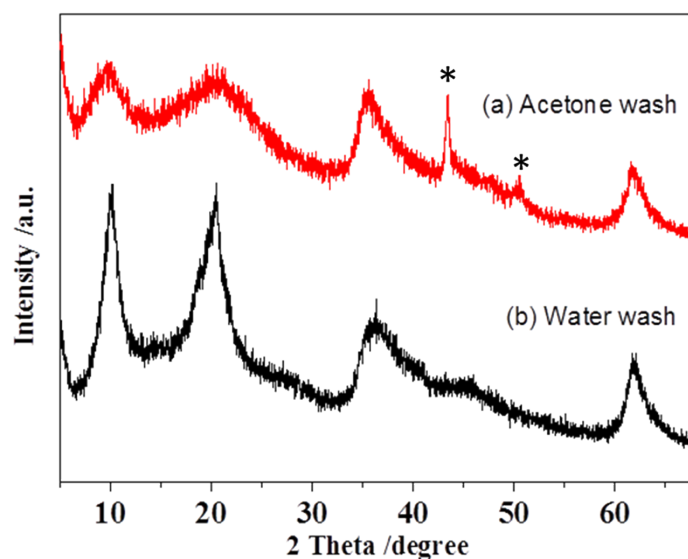


Fig. S3 XRD patterns of $\text{Mg}_3\text{Al-SO}_4\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent. (*) are Bragg reflections from the Al sample holder.

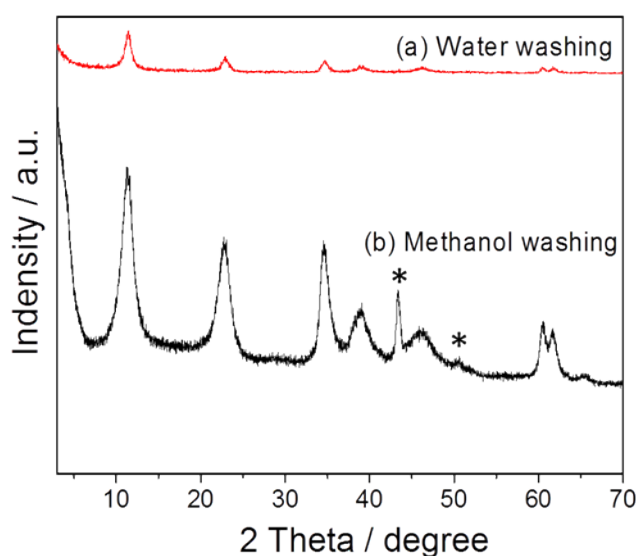


Fig. S4 XRD patterns of $\text{Mg}_3\text{Al-CO}_3\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent. (*) are Bragg reflections from the Al sample holder

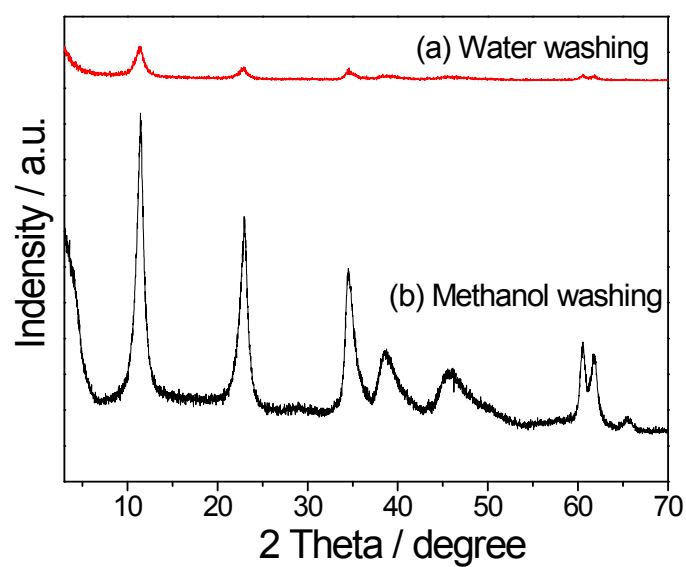


Fig. S5 XRD patterns of $\text{Mg}_3\text{Al-SO}_4\cdot 10$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent.

2.2 Infrared spectroscopy

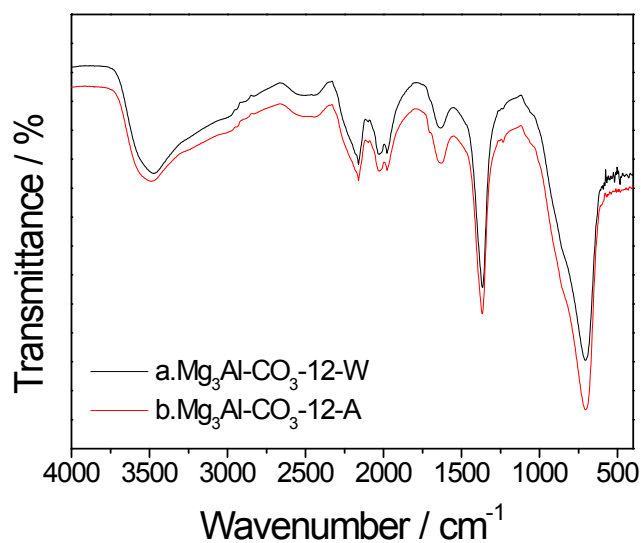


Fig. S6 FTIR patterns of $\text{Mg}_3\text{Al-CO}_3\text{-12}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

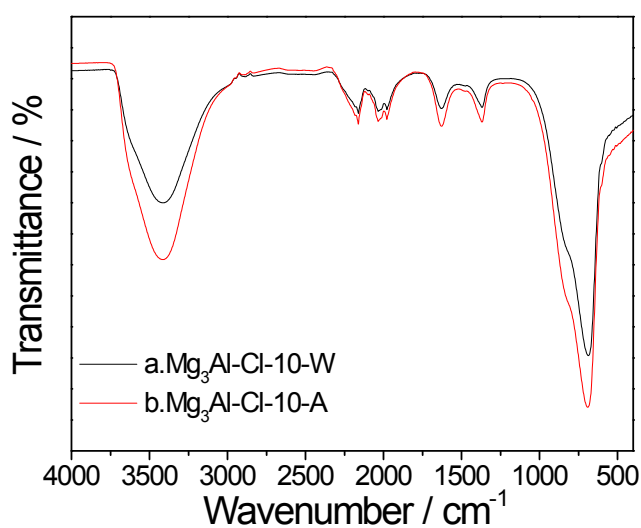


Fig. S7 FTIR patterns of $\text{Mg}_3\text{Al-Cl-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

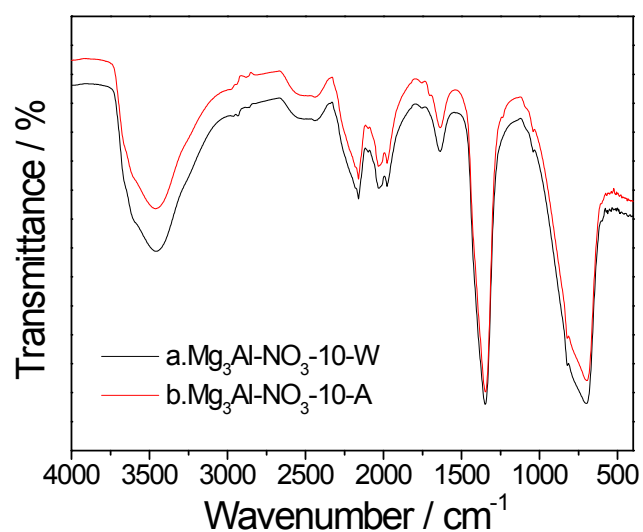


Fig. S8 FTIR patterns of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

2.3 Transmission Electron Microscopy

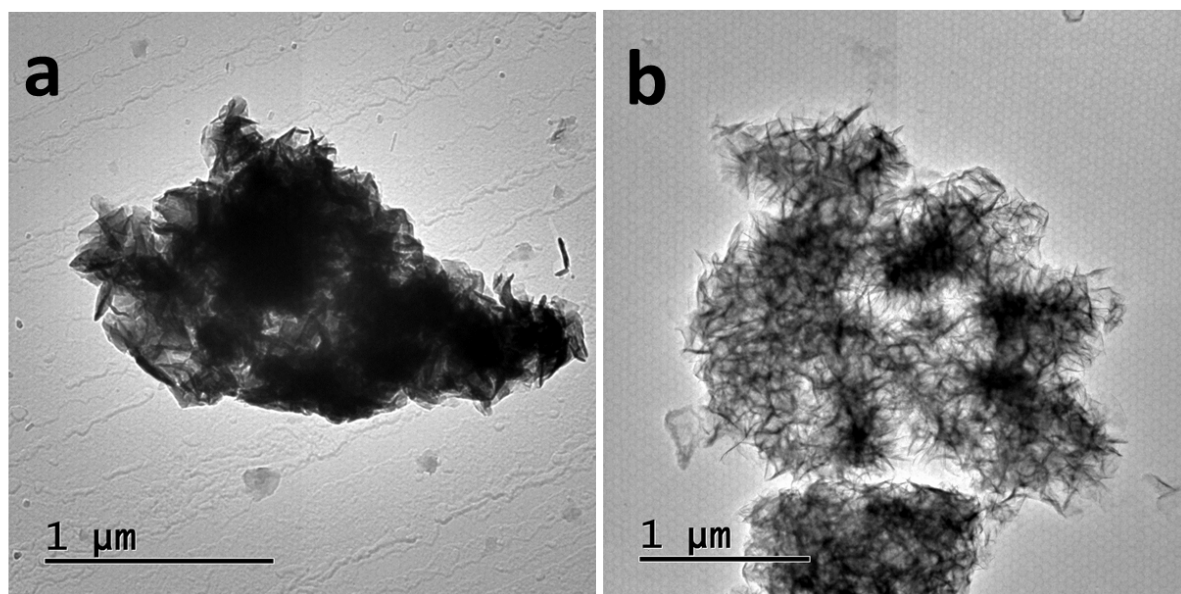


Fig. S9 TEM patterns of $\text{Mg}_3\text{Al-Cl-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

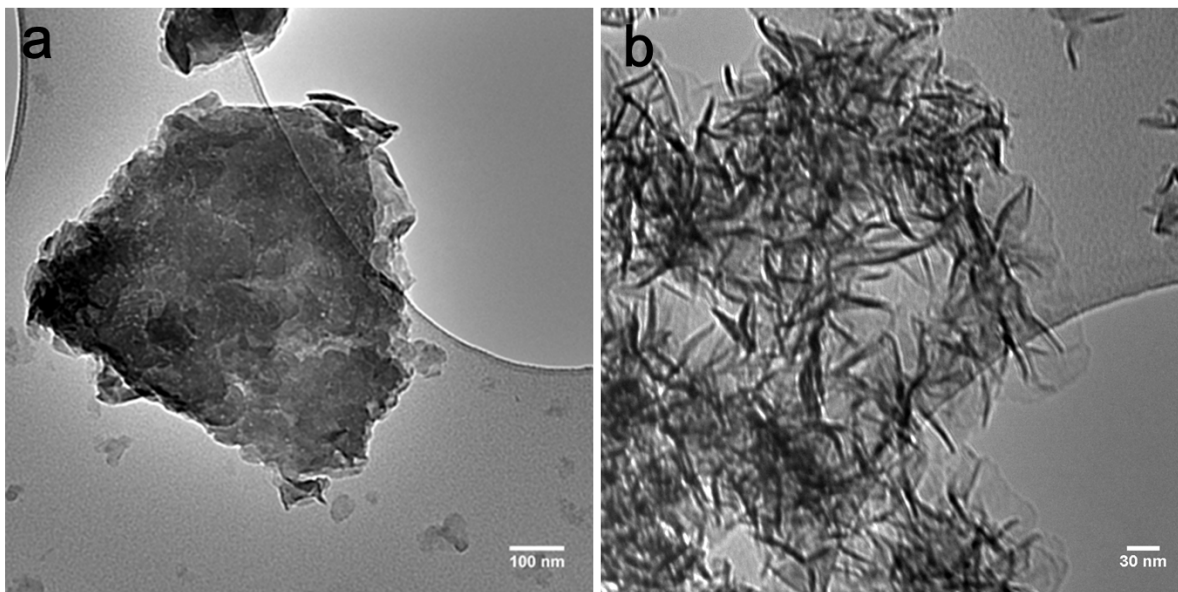


Fig. S10 TEM patterns of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

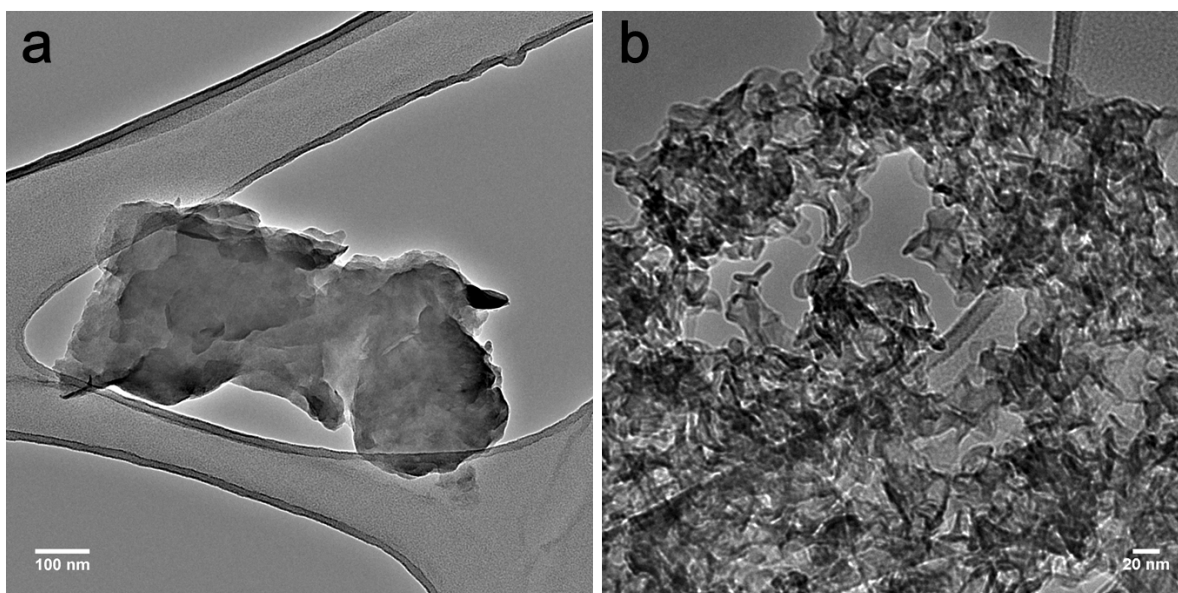


Fig. S11 TEM patterns of $\text{Mg}_3\text{Al-SO}_4\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

2.4 Scanning Electron Microscopy

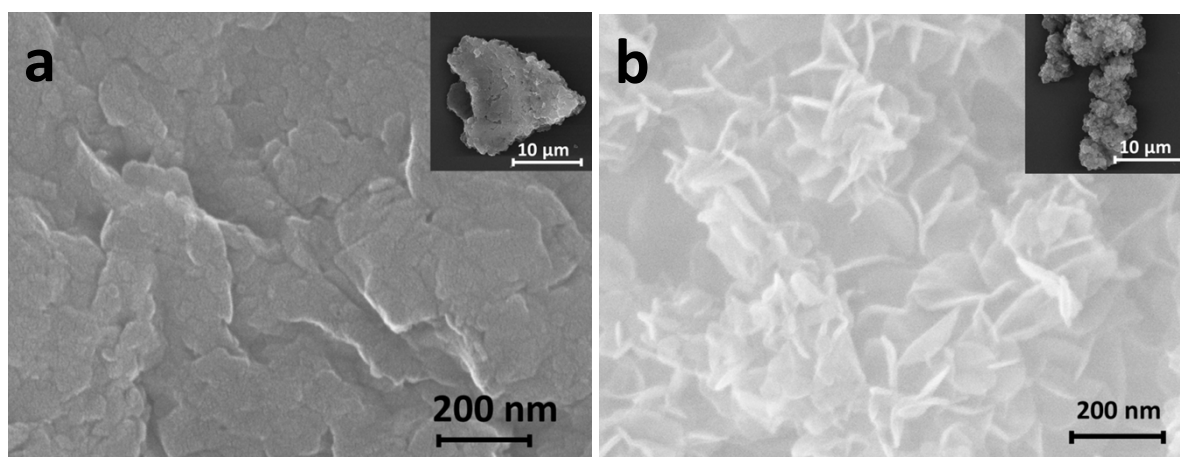


Fig. S12 TEM patterns of $\text{Mg}_3\text{Al-Cl-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

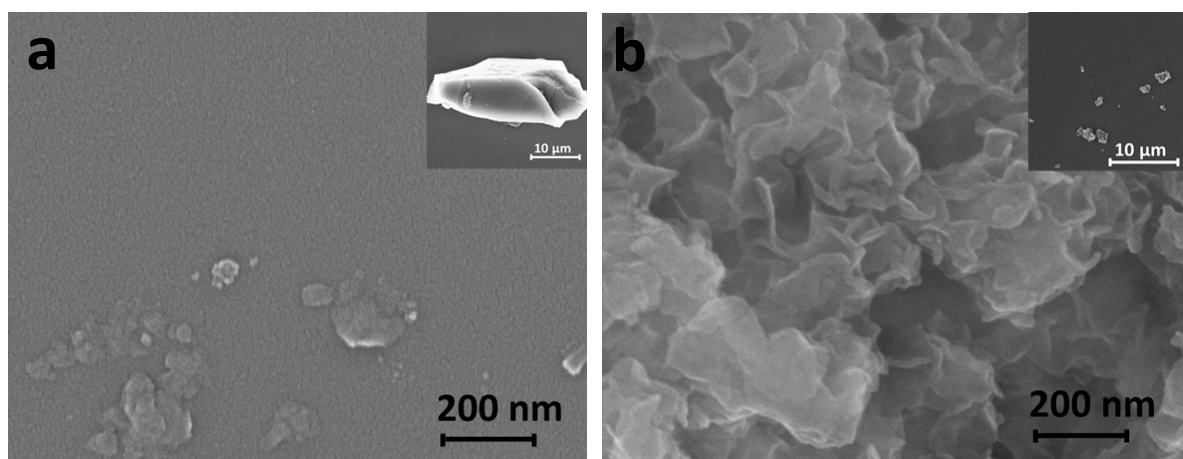


Fig. S13 TEM patterns of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

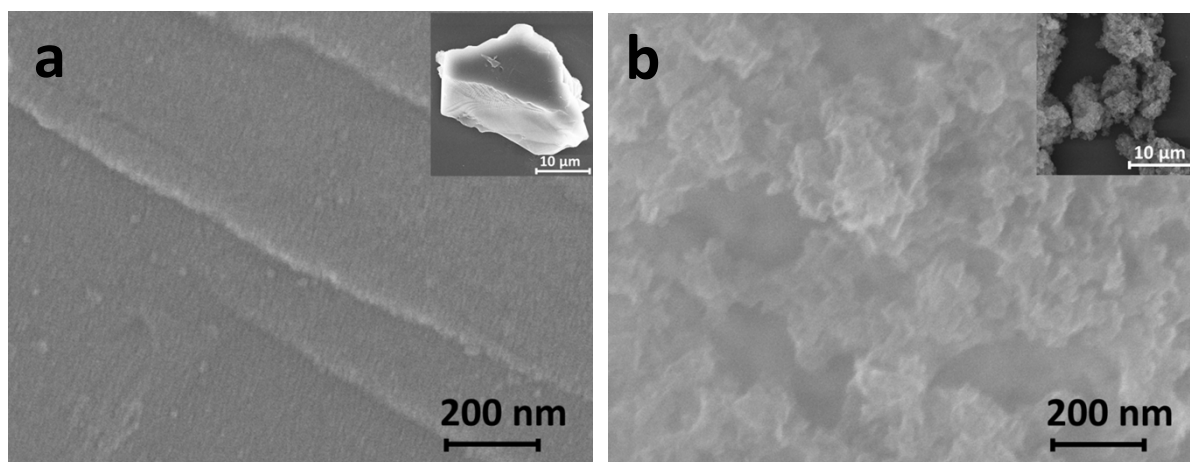


Fig. S14 TEM patterns of $\text{Mg}_3\text{Al-SO}_4\text{-10}$ (a) sample prepared by conventional co-precipitation method in water at pH 10 (b) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent.

1 2.5 Thermogravimetric analysis

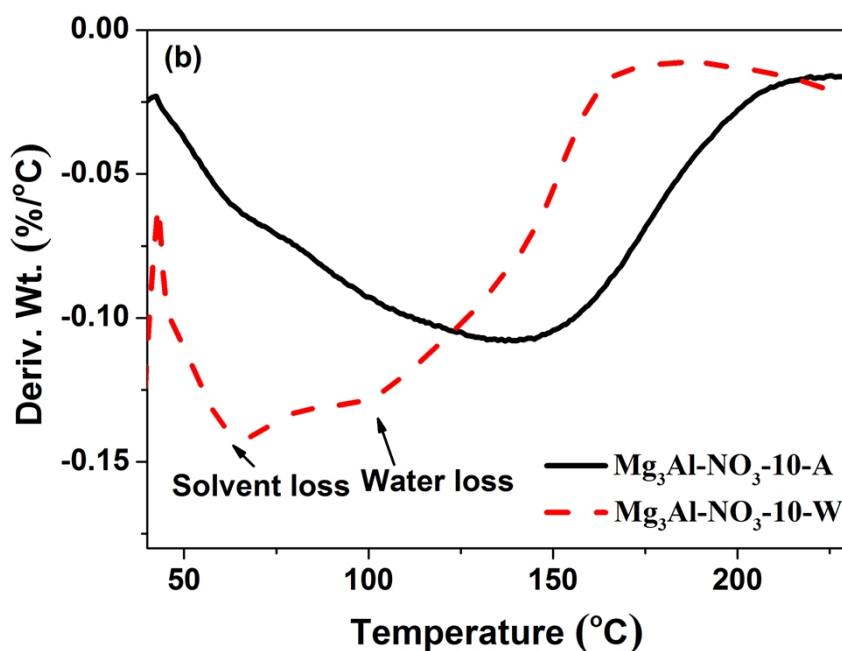
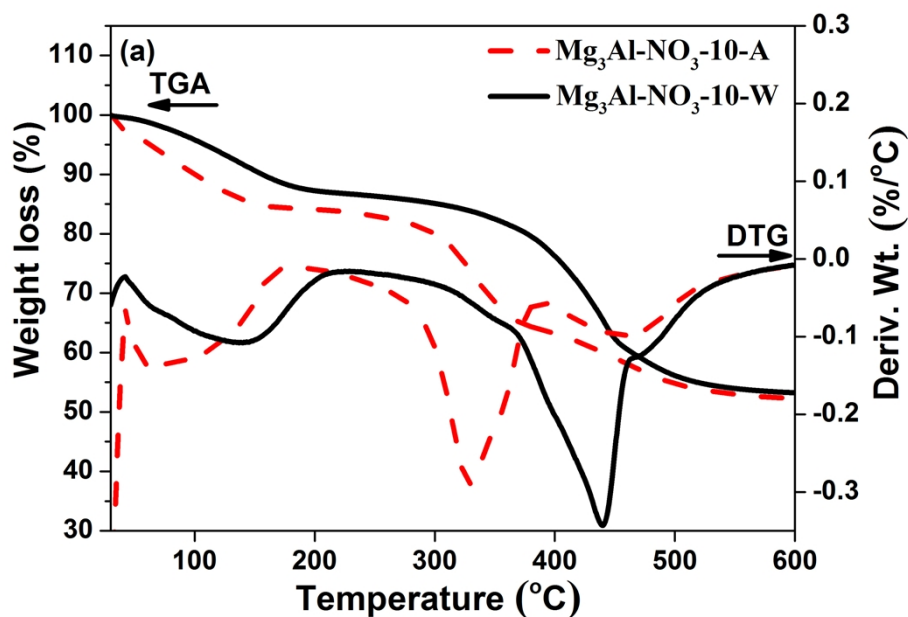


Fig. S15. TGA and DTG analysis of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ LDHs (a) in the range of 30-600 °C; (b) in the range of 30-230 °C; $\text{Mg}_3\text{Al-NO}_3\text{-10-W}$ prepared by a conventional co-precipitation method in water at pH 10. $\text{Mg}_3\text{Al-NO}_3\text{-10-A}$ is prepared by identical conditions in water at pH 10 according to the AMOST method using acetone as the AMO-solvent.

1
2 **Table S1** Summary of water and AMO-solvent content in the AMO-LDHs compared to
3 conventional C-LDHs as determined by analysis of the TGA data.

LDH	C-LDH ²		AMO-LDH-A ¹		AMO-LDH-M ¹	
	<i>b</i> ³	<i>c</i> ⁴	<i>b</i> ³	<i>c</i> ⁴	<i>b</i> ³	<i>c</i> ⁴
Mg₃Al-CO₃-10	0.41	0	0.34	0.04	--	--
Mg₃Al-CO₃-12	0.7	0	0.43	0.11	0.44	0.11
Mg₂Al-CO₃-10	1.05	0	0.59	0.18	--	--
Mg₃Al-Cl-10	0.58	0	0.46	0.04	--	--
Mg₃Al-SO₄-10	0.77	0	0.71	0.17	--	--
Mg₃Al-NO₃-10	0.57	0	0.38	0.12	--	--
Mg₃Al_{0.5}Fe_{0.5}-10	0.74	0	0.5	0.06	--	--

4 ¹AMO-LDH-A and AMO-LDH-M are the LDH with the formula of $[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/r} \cdot bH_2O \cdot c(AMO-solvent)$ (**1**); wherein M and M' are metal cations, *z* = 1 or 2; *y* = 3 or 4, 0 <
5 *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 =
6 Acetone, M = Methanol).

8 ²C-LDH is an LDH with the formula $[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/r} \cdot bH_2O$ (**2**); wherein M and
9 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
10 and *a* = *z*(1-*x*)+*xy*-2.

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

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

13

14

15

2.6 BET Analysis

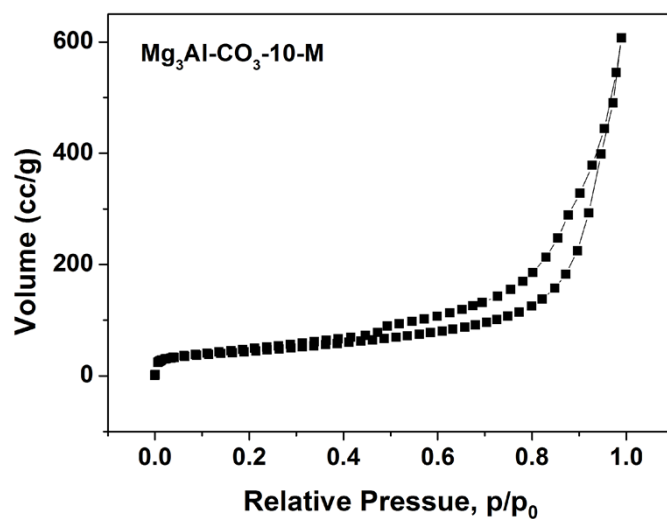


Fig. S16 BET Isotherms of $\text{Mg}_3\text{Al-CO}_3\text{-10}$ BET sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent.

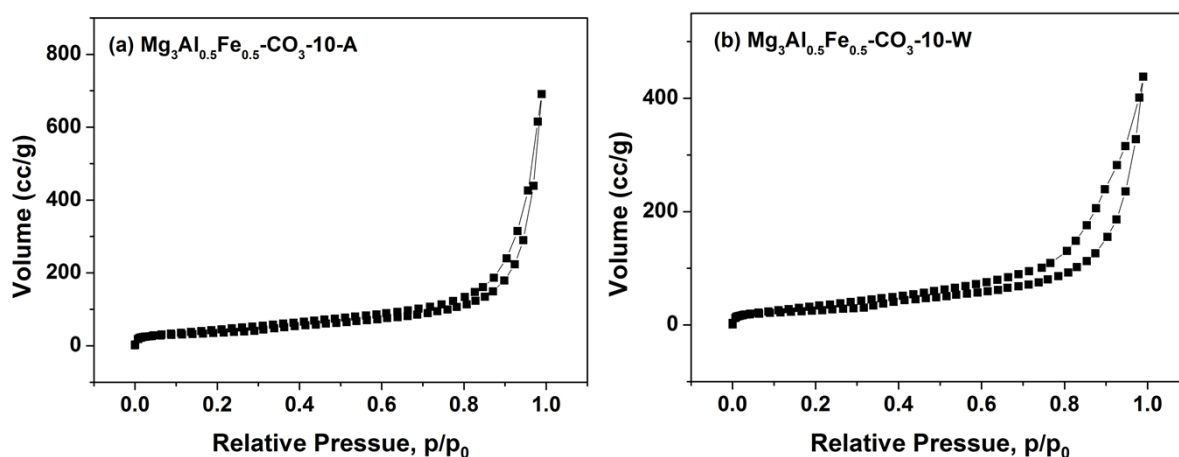


Fig. S17 BET Isotherms of $\text{Mg}_3\text{Al}_{0.5}\text{Fe}_{0.5}\text{-CO}_3\text{-10}$ (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent (b) sample prepared by conventional co-precipitation method in water at pH.

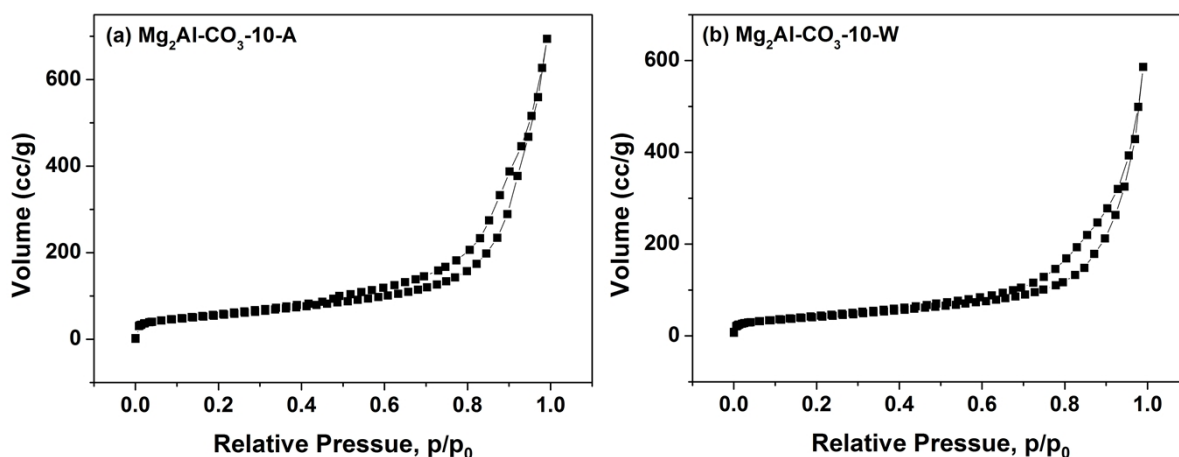


Fig. S18 BET Isotherms of $\text{Mg}_2\text{Al-CO}_3\text{-10}$ (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using acetone as the AMO-solvent (b) sample prepared by conventional co-precipitation method in water at pH 10.

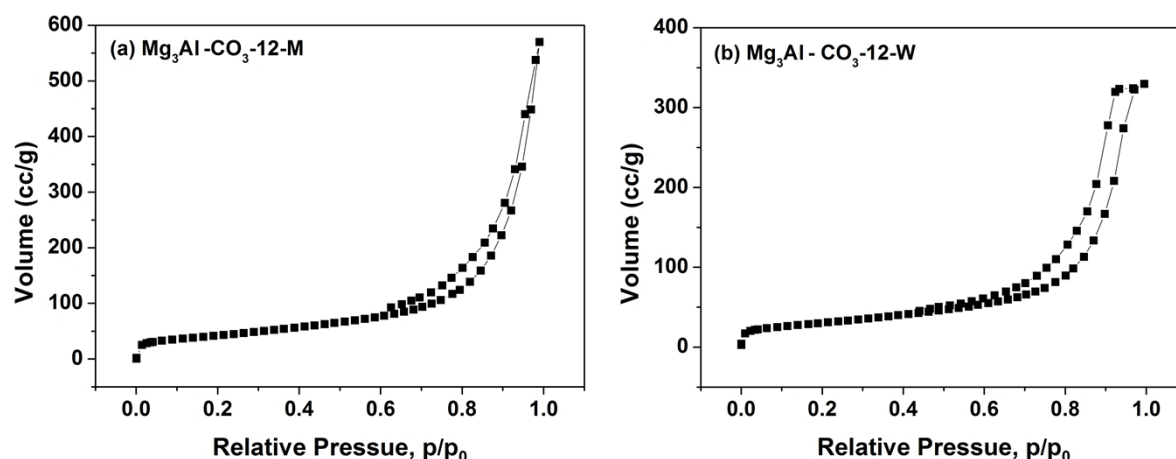
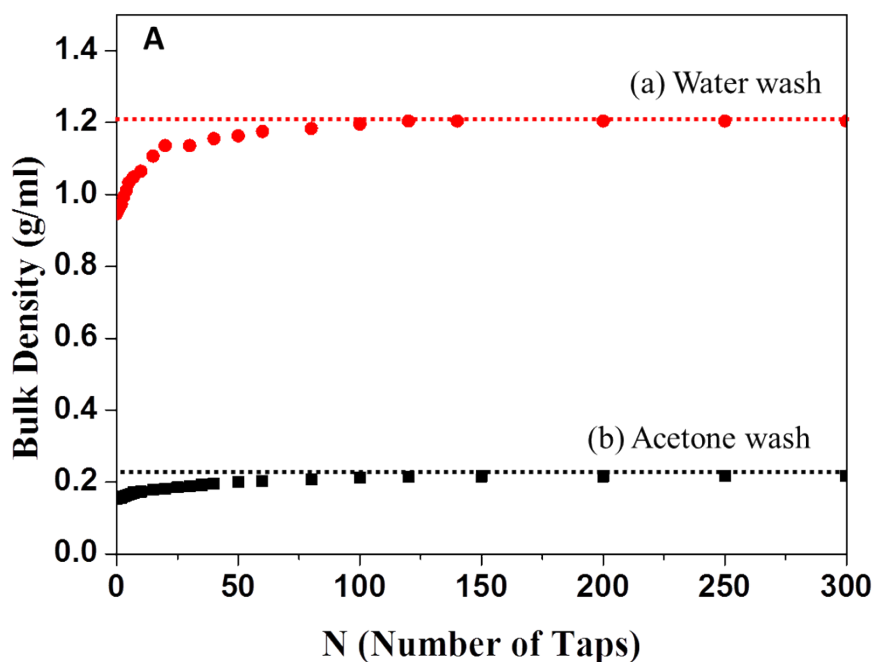
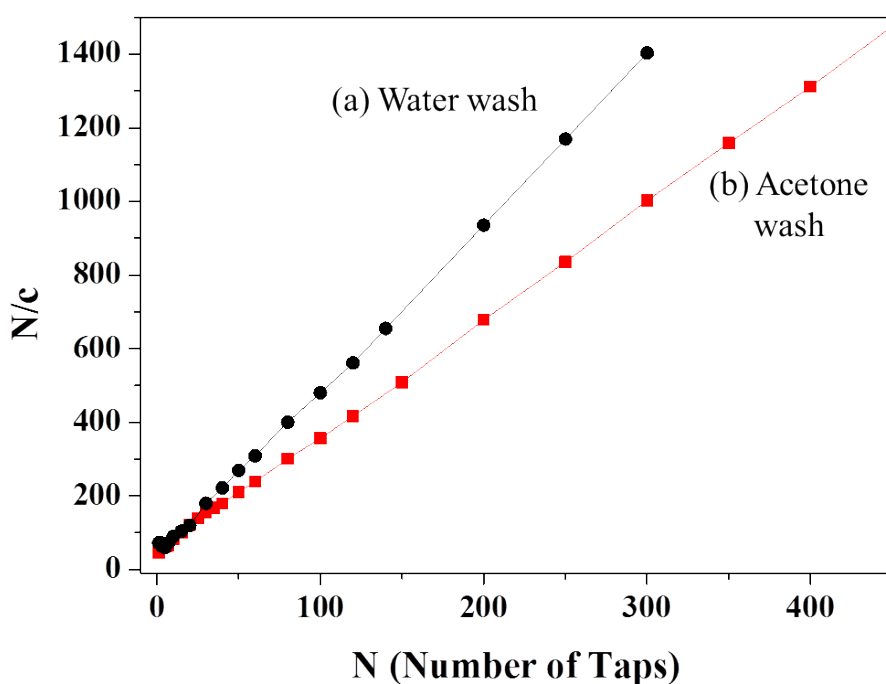


Fig. S19 BET Isotherms of $\text{Mg}_3\text{Al-CO}_3\text{-12}$ (a) sample prepared under identical synthesis conditions with the additional AMOST method treatment using methanol as the AMO-solvent (b) sample prepared by conventional co-precipitation method in water at pH 12.

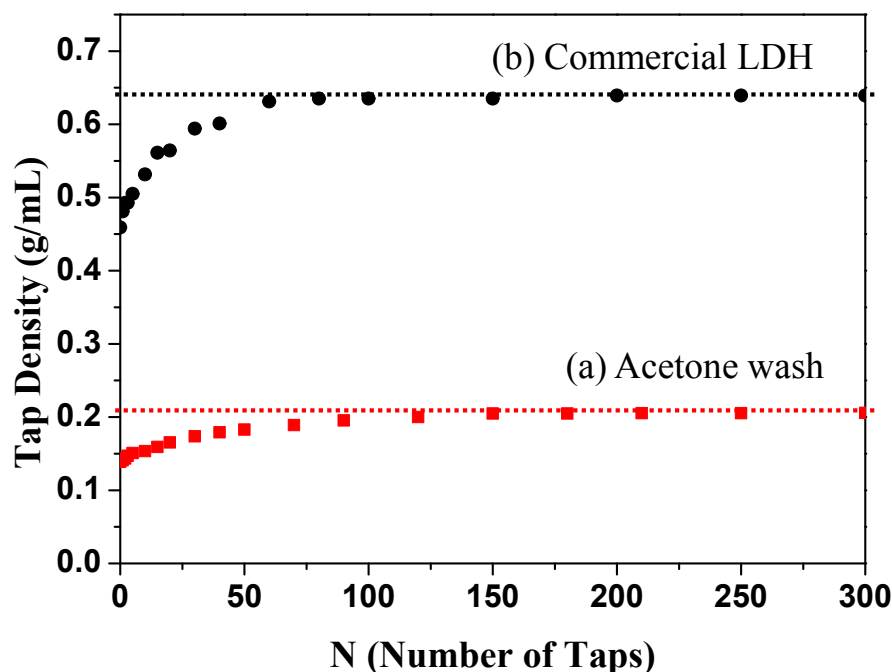
1 2.7 Density studies



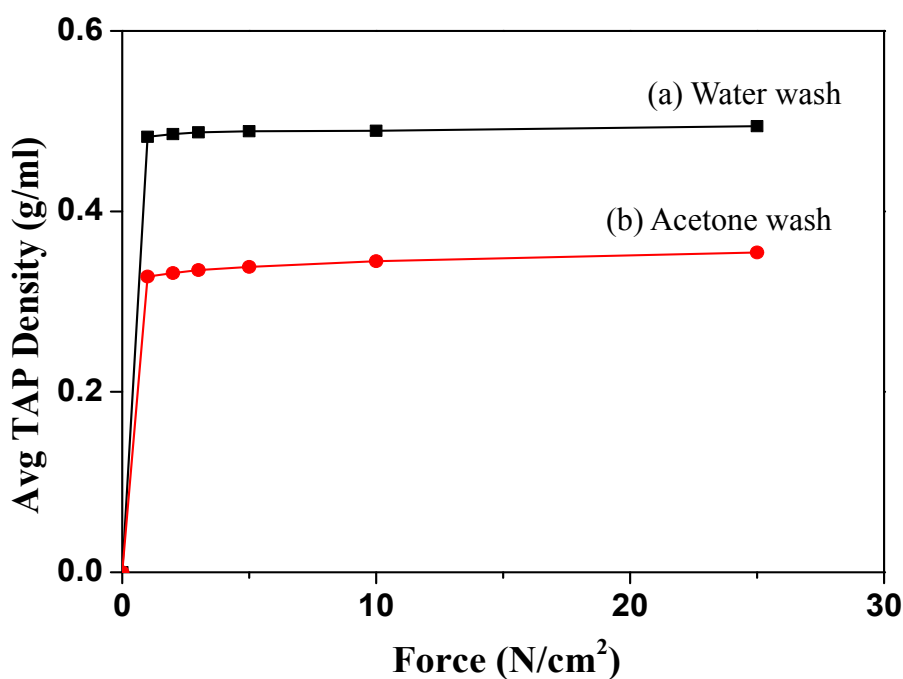
2
3 **Fig. S20** Bulk density of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ LDH; (a) sample prepared by a conventional co-
4 precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent
5 acetone.



6
7 **Fig. S21** Carr's index curves of $\text{Mg}_3\text{Al-NO}_3\text{-10}$ LDH; (a) sample prepared by a conventional
8 co-precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent
9 acetone.



1
2 **Fig. S22** Bulk density of $\text{Mg}_3\text{Al-CO}_3\text{-10 LDH}$; (a) sample prepared by a conventional co-
3 precipitation method in water at pH 10 and (b) AMOST method using the AMO-solvent
4 acetone.



5
6 **Fig. S23** GeoPyc T.A.P density of $\text{Mg}_3\text{Al-CO}_3\text{-10 LDH}$; (a) sample prepared by a
7 conventional co-precipitation method in water at pH 10 and (b) AMOST method using the
8 AMO-solvent acetone.

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