Electronic Supplementary Information

Decarbonating layered double hydroxides with carbonated salt solution

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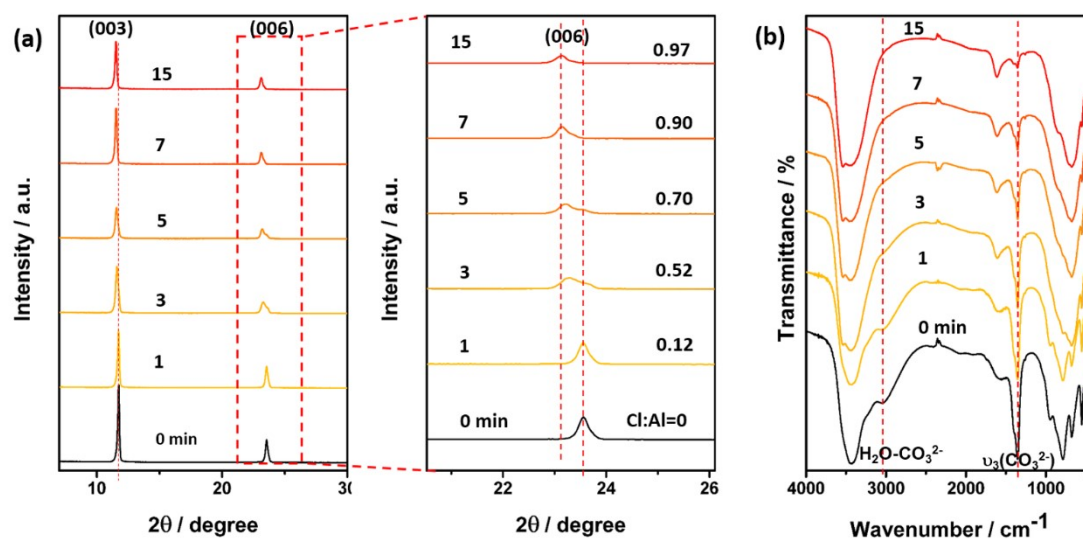*Corresponding author. E-mail address: yxwang@tju.edu.cn

Fig. S1 Decarbonation process of Mg_2Al-LDH-CO_3 by carbonated NaCl solution. (a) XRD patterns and (b) FTIR spectra as a function of reaction time. The diffraction signal from the (006) plane of Mg_2Al-LDH LDHs splits into two peaks during the decarbonation process, indicating a phase transformation from Mg_2Al-LDH-CO_3 to Mg_2Al-LDH-Cl. Furthermore, peaks assigned to CO_3^{2-} at 3000 cm^{-1} and 1360 cm^{-1} in FTIR spectra of LDHs dimed as a function of time.
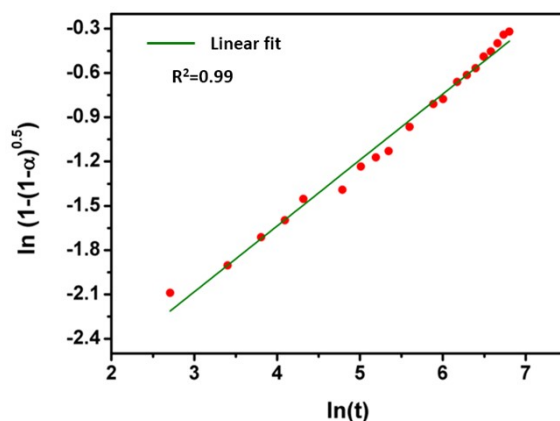
Fig. S2 Decarbonation kinetic analysis. 2D advancing interface model[1] fitted well with the decarbonation of MgAl-LDH by carbonated NaCl solution. The reaction extent α (Cl/Al ratio in LDHs) of decarbonation process is associated with the increment of carbonate in the solution, and t represents the reaction time. The exact increment of carbonate in decarbonation system was calculated from the dissociation equilibrium constant of H_2CO_3-HCO_3^--CO_3^{2-} and real-time pH value in **Fig. 1b**. The decarbonation kinetic demonstrate that the decarbonation reaction advances along the channel. The coexistence of Mg_2Al-LDH-CO_3 and Mg_2Al-LDH-Cl phase in **Fig. S1** during the initial stage of the decarbonation process is also in line with the advancing interface model.
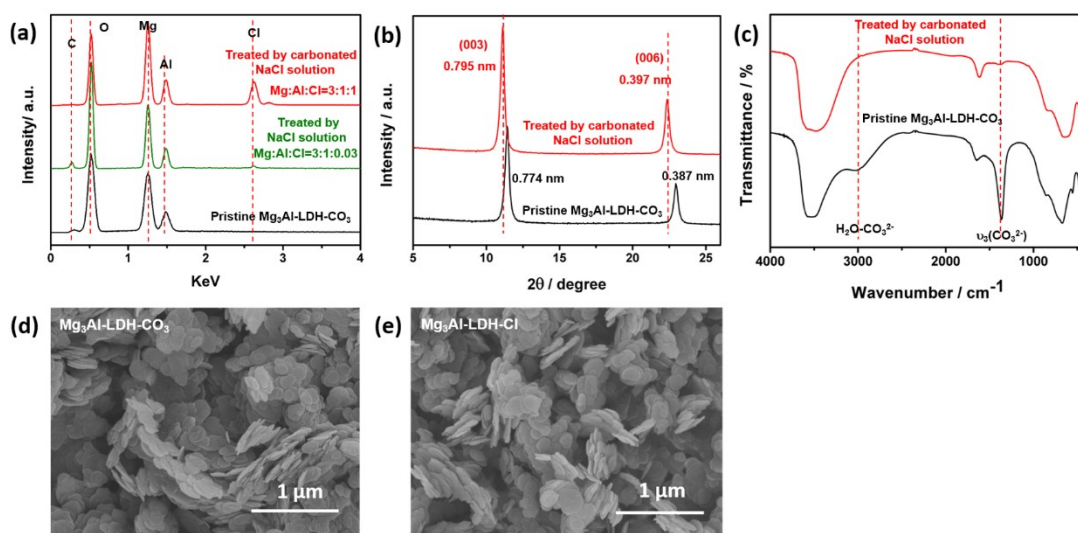

Fig. S3 (a) EDS spectra indicating complete decarbonation of Mg_3Al-LDH-CO_3; (b) XRD patterns showing the peak shift and d-spacing change from Mg_3Al-LDH-CO_3 to Mg_3Al-LDH-Cl; (c) FTIR spectra showing the disappearance of CO_3^{2-} vibration peaks; (d & e) SEM images indicating well-kept morphology of Mg_3Al-LDH after anion exchange from CO_3^{2-} to Cl^-.
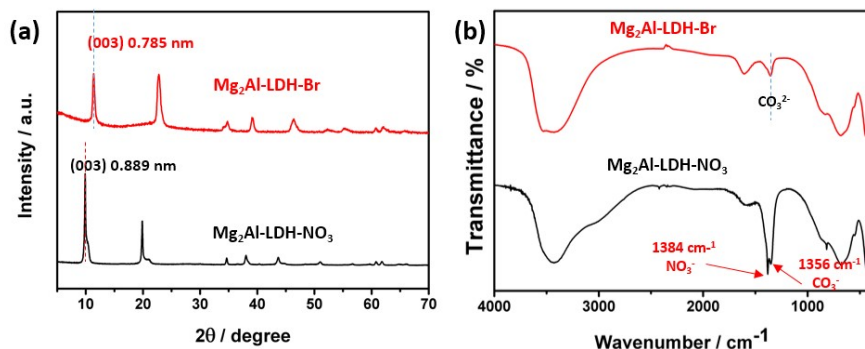
Fig. S4 Decarbonation of $Mg_2Al\text{-}LDH\text{-}CO_3$ by carbonated $NaNO_3$ and $NaBr$ solution. (a) XRD patterns (b) FTIR spectra of $Mg_2Al\text{-}LDH\text{-}Br$ and $Mg_2Al\text{-}LDH\text{-}NO_3$. The peak at 1356 cm^{-1} is attributed to the residual CO_3^{2-} in LDHs.
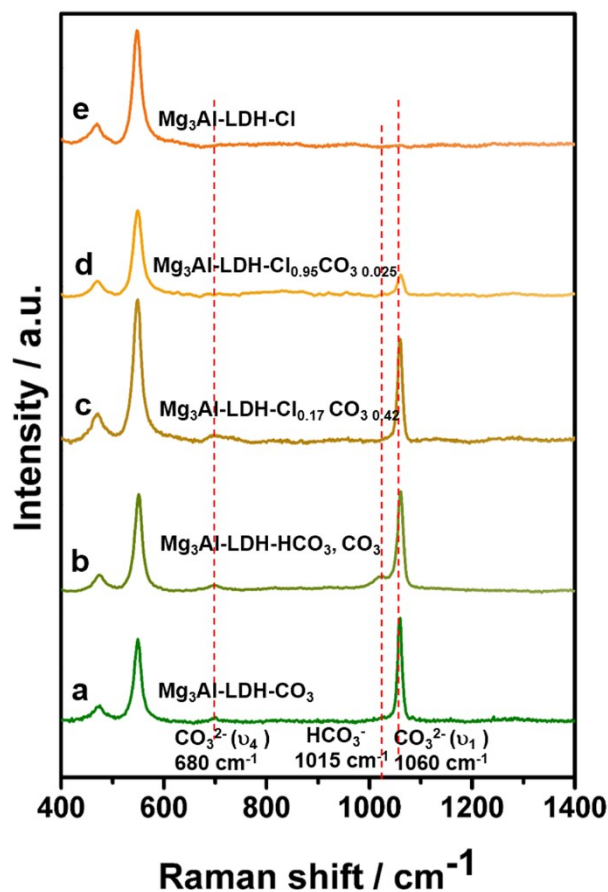
Fig. S5 Raman spectra of (a) pristine $Mg_3Al\text{-}LDH\text{-}CO_3$, (b) $Mg_3Al\text{-}LDH\text{-}CO_3$ treated with carbonated water, (c) $Mg_3Al\text{-}LDH$ first treated with carbonated water then NaCl solution, (d) pristine $Mg_3Al\text{-}LDH\text{-}CO_3$ treated with carbonated NaCl solution for 8 minutes and (e) pristine $Mg_3Al\text{-}LDH\text{-}CO_3$ treated with carbonated NaCl solution for two rounds. In contrast to CO_3^{2-}, HCO_3^- in LDHs can be easily substituted by Cl$^-$. After MgAl-LDH intercalated with HCO_3^- was treated with NaCl solution, the Cl/Al ratio of LDHs is 0.17. In addition,

the absence of HCO_3^- in LDHs during the decarbonation process demonstrates that almost all of the HCO_3^- in LDHs are substituted by Cl^-. The residual anion in LDHs is only CO_3^{2-}, confirming MgAl-LDH-HCO_3 with higher anion-exchange ability than that of MgAl-LDH-CO_3.
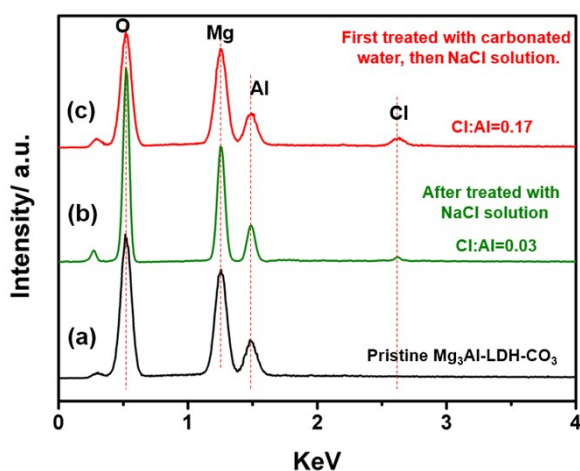

Fig. S6 EDS spectra of (a) pristine Mg_3Al-LDH-CO_3, (b) Mg_3Al-LDH-CO_3 treated with only NaCl solution, (c) Mg_3Al-LDH first treated with carbonated water, then treated with NaCl solution. Massive Cl was detected after LDH intercalated with HCO_3^- was treated with NaCl solution.
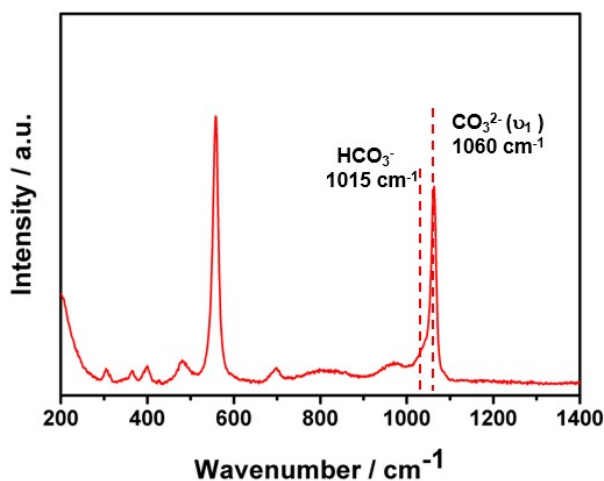

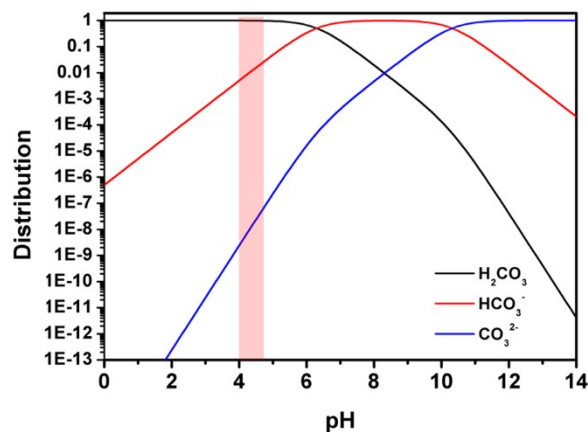**Fig. S7** Raman spectrum of Mg_2Al-LDH-CO_3 treated with carbonated water.

Fig. S8 Distribution coefficient of H_2CO_3-HCO_3^--CO_3^{2-} as a function of pH. Although CO_3^{2-} is always accompanied by HCO_3^- because of the dissociation equilibrium, CO_3^{2-} was dramatically depressed in carbonated water, and the content of CO_3^{2-} is in the range of $10^{-7} \sim 10^{-9}$.

Tab. S1. Hydration energy for various anions.[2]

Anion	Hydration energy / kJ mol^{-1}
CO_3^{2-}	-1315
OH^-	-430
F^-	-465
Cl^-	-340
HCO_3^-	-335
Br^-	-315
NO_3^-	-300
I^-	-275

References

1. L. Palin, M. Milanesio, W. van Beek and E. Conterosito, *J. Nanomater.*, 2019, **2019**, 1-9.

2. Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2995-2999.