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Controllable luminescence of a Li-Al layered double hydroxide used as a sensor for reversible sensing of carbonate

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Table S1. The concentrations and pH values of alkaline aqueous solution with Li⁺ and Al³⁺ ions for producing LDH powder and thin film.

Material	Mass of IMC in DI water	Content (ppm)		pH
		Li ⁺	Al ³⁺	
For producing powder	0.2 g/100 ml	308.25	618.21	12.7
For producing thin film	0.1 g/200 ml	83.75	167.72	12.2

Table S2 The cations contents on the positively charged layer in three powders Li-Al-CO₃ LDH, LDH/900 °C_Cal and LDH/300 °C_Cal were examined by ICP-OES analysis

Sample	Content (ppm)		
	Li ⁺	Al ³⁺	Fe ³⁺
Li-Al-CO ₃ LDH	33.90	256.84	0.07
LDH/900 °C_Cal	26.60	119.00	0.23
LDH/300 °C_Cal	47.30	335.84	0.14

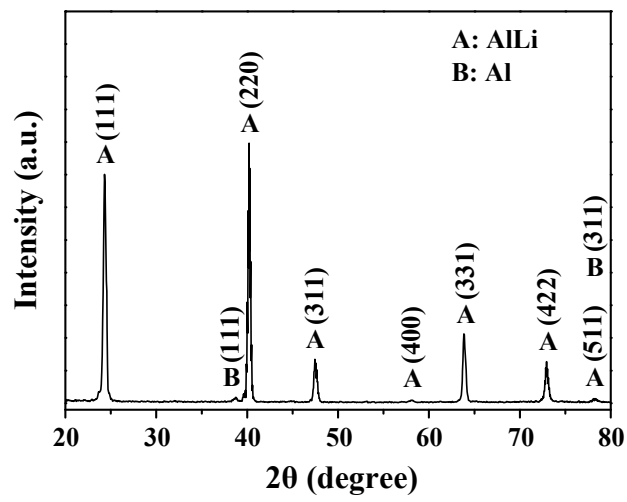


Fig. S1 XRD pattern of AlLi intermetallic compound (IMC).

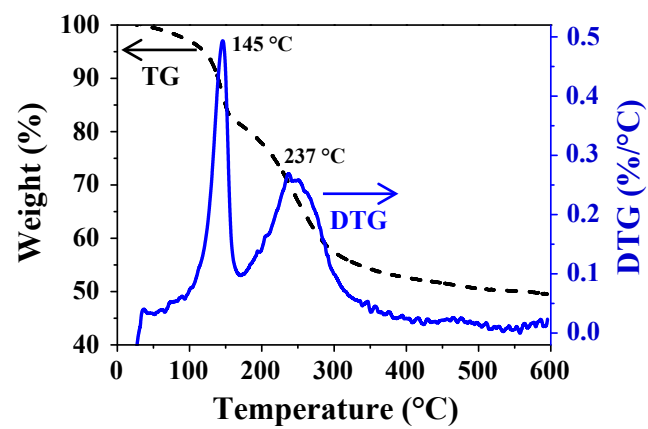


Fig. S2 TG-DTG curves of the Li-Al-CO₃ LDH powder.

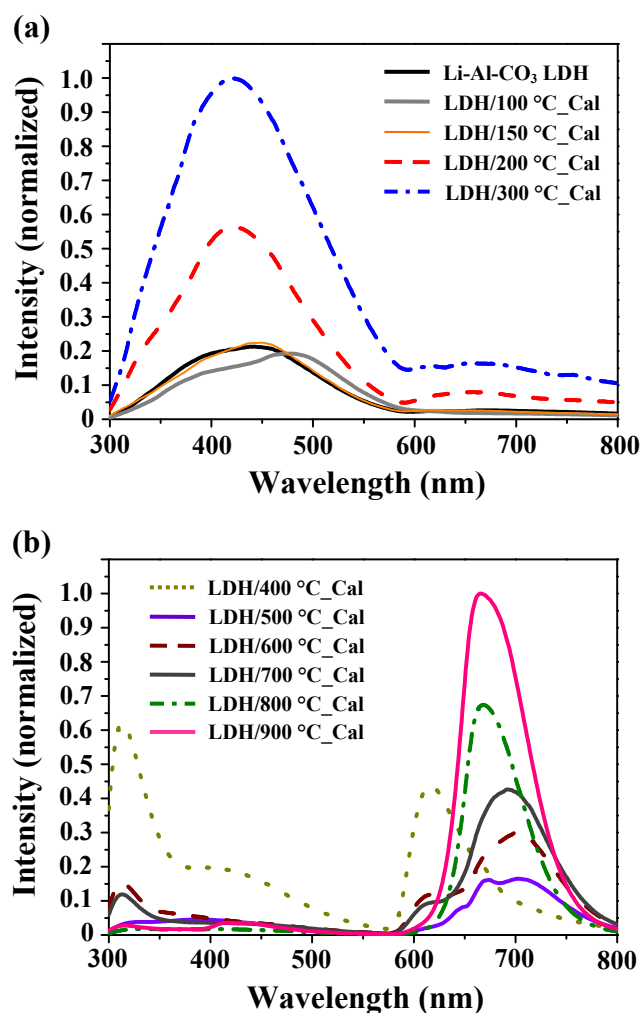


Fig. S3 Room temperature photoluminescence emission spectra at various calcination temperature: (a) Li-Al-CO₃ LDH, LDH/100 °C_Cal, LDH/150 °C_Cal, LDH/200 °C_Cal and LDH/300 °C_Cal powder; (b) LDH/400 °C_Cal, LDH/500 °C_Cal, LDH/600 °C_Cal, LDH/700 °C_Cal, LDH/800 °C_Cal and LDH/900 °C_Cal powder. (a) and (b) were using an excitation wavelength of 280 nm.

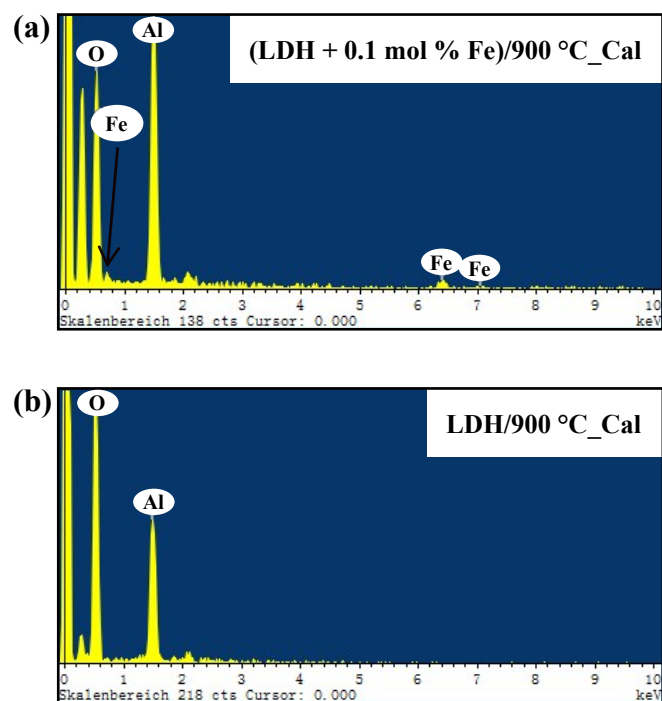


Fig. S4 EDS spectra showing the evidence of Fe ions in the (LDH + 0.1 mol % Fe)/900 °C_Cal material: (a) the EDS analysis of the compound of the LDH + 0.1 mol % Fe that was calcined at 900 °C (denoted as (LDH + 0.1 mol % Fe)/900 °C_Cal); (b) for comparison, the EDS analysis of LDH/900 °C_Cal (un-doped by Fe ions).

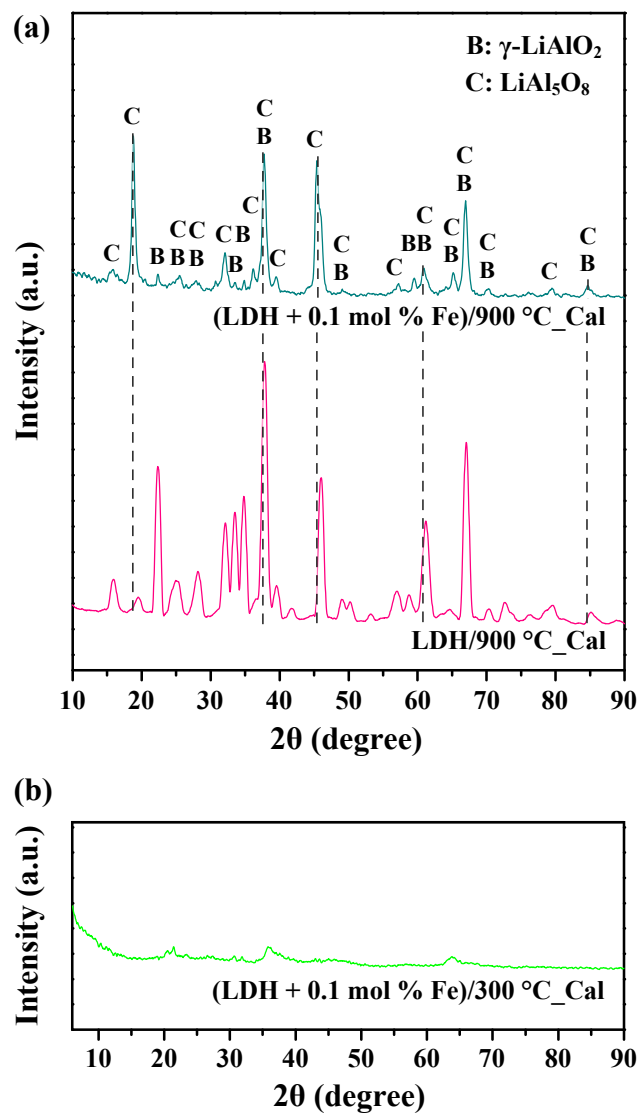


Fig. S5 XRD patterns of: (a) LDH/900 °C_Cal and (LDH + 0.1 mol % Fe)/ 900 °C_Cal; (b) (LDH + 0.1 mol % Fe)/300 °C_Cal.

In Fig. S6a, the pink solid line is the PL spectrum of LDH/900 °C_Cal, which was shown previously in Fig. 4d. When the LDH/900 °C_Cal powder was calcined at 300 °C for 3 hours, sample LDH/900 °C_Cal at 300 °C was obtained, whose PL spectrum is presented as the gray dotted line in Fig. S6a. Evidently, heat-treating LDH/900 °C_Cal at 300 °C barely changed the intensity of red emission by sample LDH/900 °C_Cal. However, calcination of the mixture of LDH/900 °C_Cal powder and 0.1 mol % Fe (from aqueous Fe(NO₃)₃) at 300 °C was carried out to form (LDH/900 °C_Cal + 0.1 mol % Fe)/300 °C_cal sample. The calcined compound emitted almost zero red light, as revealed by the blue solid line in Fig. S6a. With reference to Fig. 7a, the sample (LDH + 0.1 mol % Fe)/ 900 °C_cal that was produced by calcination of the mixture of LDH powder and 0.1 mol % Fe at 900 °C emitted intense red luminescence. Importantly, when LDH/900 °C_Cal powder was calcined at 300 °C, it continued to emit intense red light (gray dotted line in Fig. S6a). Therefore, heating at 300 °C was not the cause of low red emission intensity; rather, superficial Fe³⁺ was. When sample (LDH/900 °C_Cal + 0.1 mol % Fe) was calcined at 300 °C, the superficial Fe³⁺ concentration was higher than that of Fe³⁺ in the volumetric lattice due to low diffusion rate of Fe³⁺ in LDH. Calcination at 900 °C yielded an opposite result that increased the Fe³⁺ concentration in the volumetric lattice. Hence, an incorrect doping temperature may produce concentrated dopant ions in the superficial region, greatly reducing the red emission intensity of a mixture of LiAlO₂ and LiAl₅O₈ compounds. Fig. S6b verifies the effect of superficial Fe³⁺ concentration on lowering photoluminescence emission intensity. Li-Al-CO₃ LDH that was calcined at 300 °C (LDH/300 °C_Cal), previously shown in Figs. 4c and 7b, emitted the most intense blue luminescence of any of the calcined samples. LDH with 0.001 mol % Fe that was calcined at 300 °C ((LDH + 0.001 mol % Fe)/300 °C_Cal) exhibited lower blue emission intensity (green solid line in Fig. S6b). The blue emission intensity of LDH with 0.01 mol % Fe that was calcined at 300 °C ((LDH + 0.01 mol % Fe)/300 °C_Cal) was even lower (orange solid line in Fig. S6b) than that of (LDH + 0.001 mol % Fe)/300 °C_Cal. Calcination at 300 °C of LDH that was doped with up to 0.1 mol % Fe³⁺ to yielded (LDH + 0.1 mol % Fe)/300 °C_Cal did not exhibit any blue photoluminescence, as indicated by the cyan dotted line in Fig. S6b. Fig. S6c shows the PL emission spectra of samples (LDH + 0.1 mol % Fe)/300 °C_Cal at 300 °C for 720 hours and 3 hours, obtained under an excitation wavelength of 280 nm. As presented in Fig. S6c, the sample that was calcined for 3 hours exhibited no photoluminescence in the range 600 ~ 800 nm.

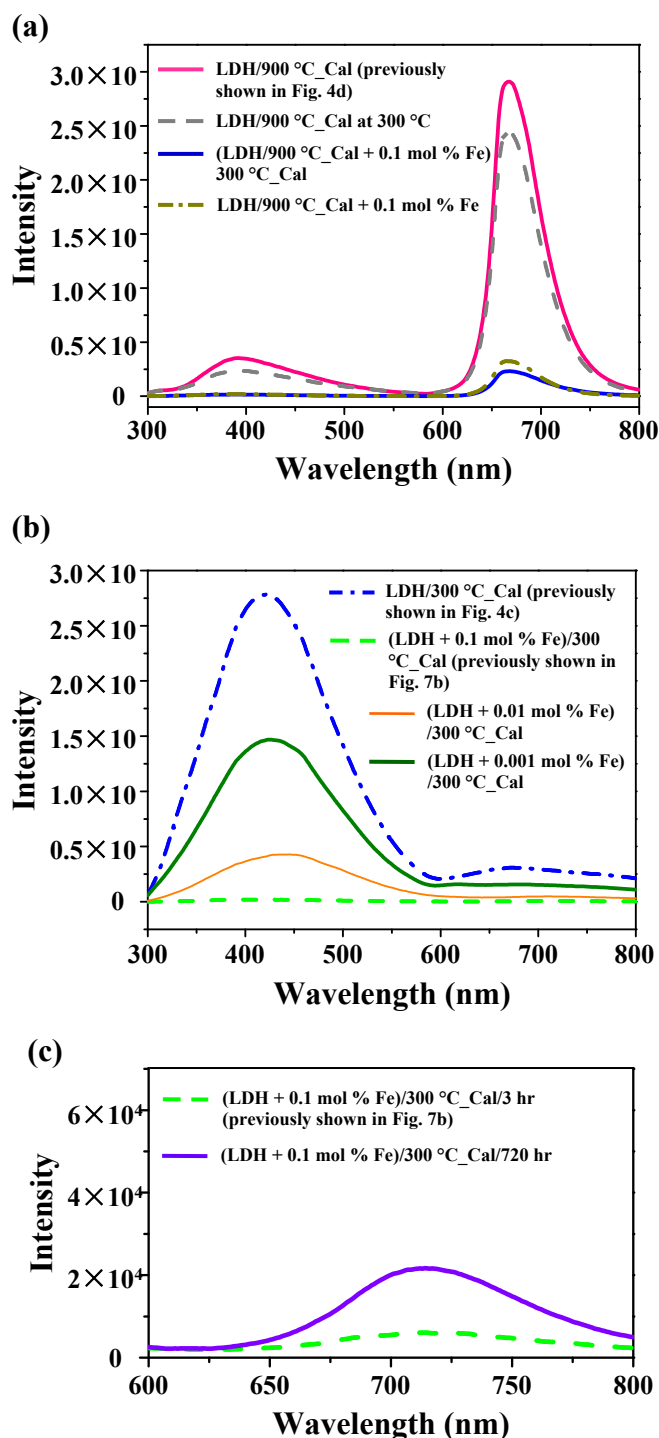


Fig. S6 (a) PL emission spectra of samples LDH/900 °C_Cal, LDH/900 °C_Cal at 300 °C, (LDH/900 °C_Cal + 0.1 mol % Fe)/300 °C_Cal and LDH/900 °C_Cal + 0.1 mol % Fe; (b) PL emission spectra of the Li-Al-CO₃ LDH powder and the LDH powders added with various Fe³⁺ concentrations, calcined at 300 °C for 3 hr; (c) PL emission spectra of (LDH + 0.1 mol % Fe)/300 °C_Cal/3hr and (LDH + 0.1 mol % Fe)/300 °C_Cal/720 hr. All of the PL emission spectra were obtained using excitation wavelength of 280 nm. For comparison, the PL spectra of the LDH/900 °C_Cal powder from Fig. 4d, LDH/300 °C_Cal powder from Fig. 4c and (LDH + 0.1 mol % Fe)/300 °C_Cal powder from Fig. 7b were replotted in (a)-(c), respectively.

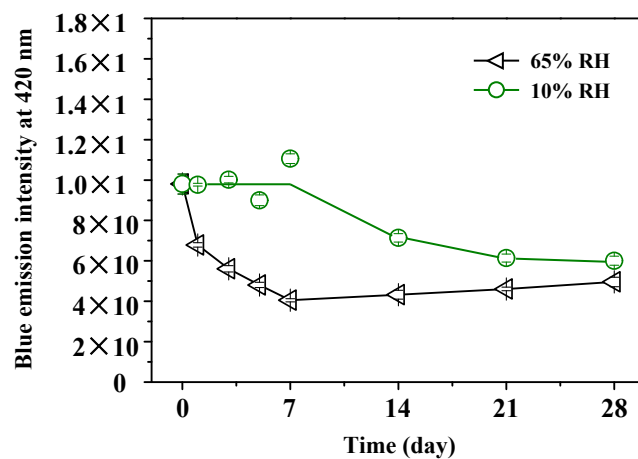


Fig. S7 Blue emission intensity: each datum point from the PL spectrum of each of the LDH/300 °C_Cal samples that were respectively stored in 10% RH and 65% RH chambers at 25 °C from 0 to 28 days. The day zero represents that the sample is an as-calcined LDH/300 °C_Cal powder. The maximum blue emission intensity of each sample was around 420 nm, under excitation wavelength of 280 nm.

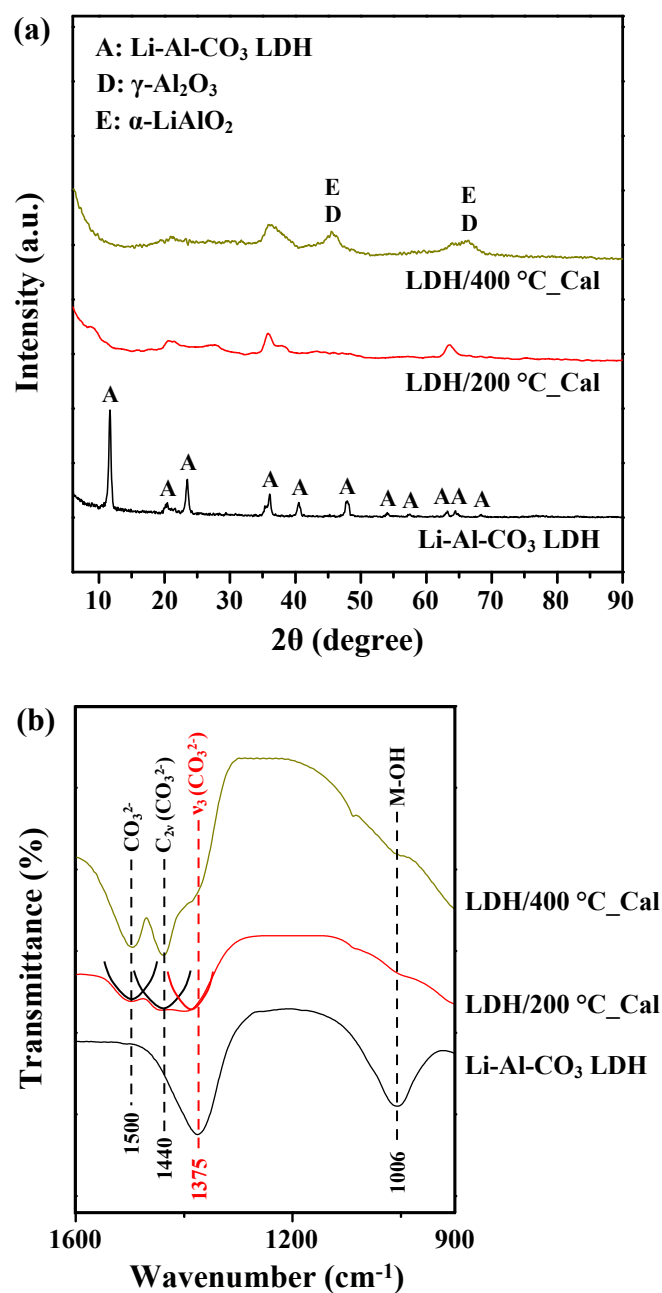


Fig. S8 XRD and FT-IR patterns of the Li-Al-CO₃ LDH, LDH/200 °C_Cal and LDH/400 °C_Cal powders were respectively displayed in Figure (a) and (b). For comparison, the patterns of Li-Al-CO₃ LDH powder previously shown in Figs. 2 and 8 were replotted in (a) and (b).

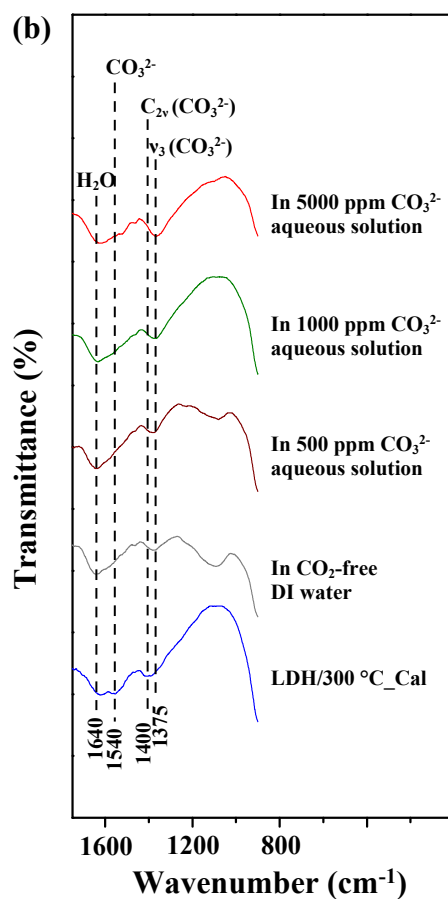
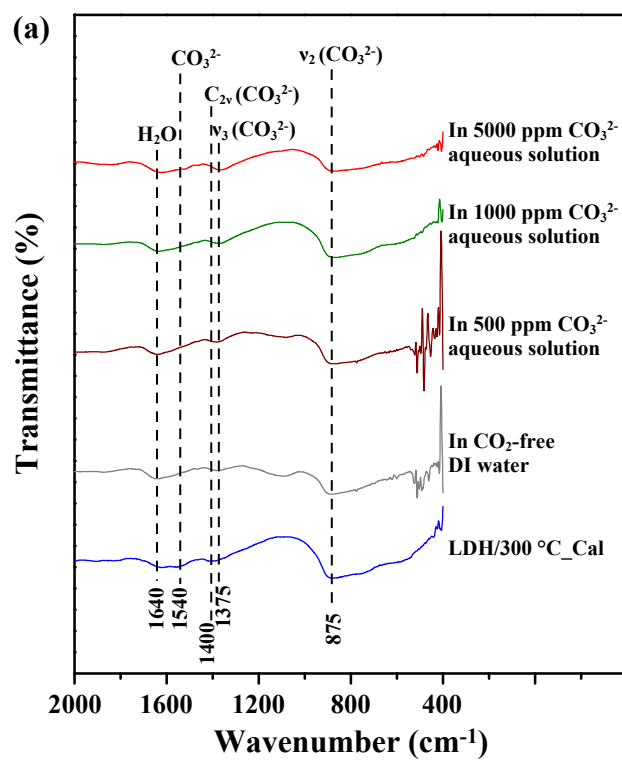


Fig. S9 (a) FT-IR spectra of the LDH/300 °C_Cal thin film and the thin film immersed in the aqueous solution with various CO_3^{2-} concentrations. (b) FT-IR spectra are zoom-in from Fig. S9a.

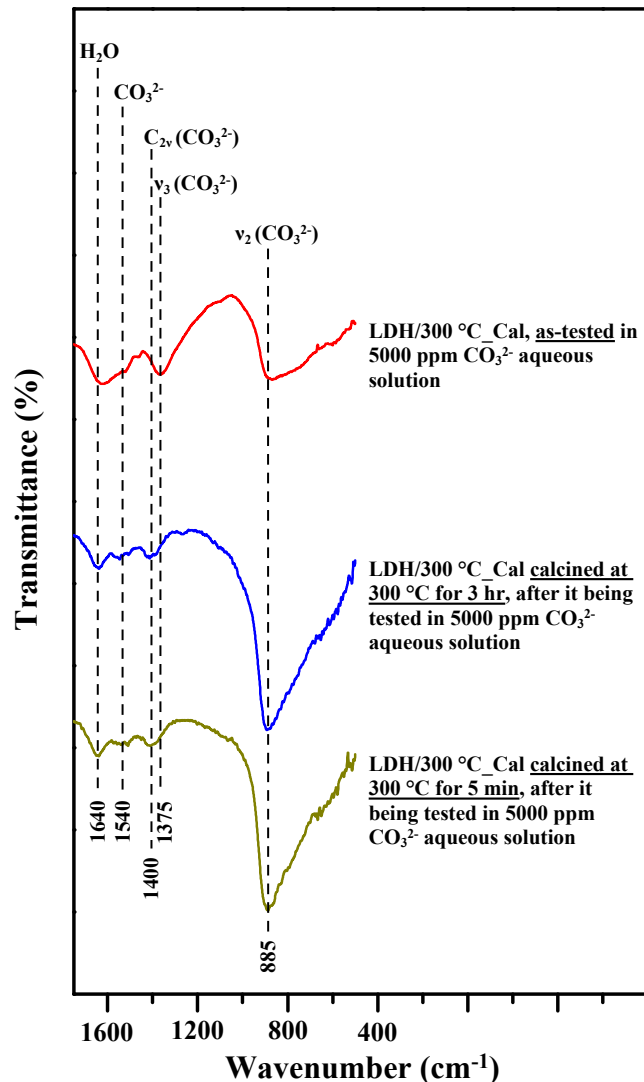


Fig. S10 FT-IR spectra of the LDH/300 °C_Cal thin film that was as-tested in 5000 ppm CO₃²⁻ aqueous solution (the upper spectrum); the middle spectrum: 3 hours calcination at 300 °C for LDH/300 °C_Cal thin film sample after it being tested in 5000 ppm CO₃²⁻ aqueous solution; and the bottom spectrum: 5 minutes calcination at 300 °C for LDH/300 °C_Cal thin film sample after it being tested in 5000 ppm CO₃²⁻ aqueous solution.