

# **Mg-Al-carbonate layered double hydroxides as a novel catalyst of luminol chemiluminescence**

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## **Experimental**

### **Chemicals and Solutions**

Analytical grade chemicals including  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  were purchased from Beijing Chemical Reagent Company and used without further purification. A 0.01 M stock solution of luminol (3-Aminophthalhydrazide) was prepared by dissolving luminol (Acros) in 0.1 M sodium hydroxide solution without purification, and was used after about two weeks in order to make luminol more stable. Working solutions of luminol were prepared by diluting the stock solution with deionized water (Milli-Q, Millipore). Working solutions of  $\text{H}_2\text{O}_2$  were prepared daily from 30% (v/v)  $\text{H}_2\text{O}_2$  (Beijing Chemical Reagent Company, China). The deionized and de- $\text{CO}_2$  water was used in all of these experimental processes.

### **Synthesis of Mg-Al- $\text{CO}_3$ LDHs**

LDHs with Mg-Al in the layers ( $\text{Mg}^{2+}/\text{Al}^{3+}$ ) and carbonate in the interlayers were prepared by the coprecipitation method at constant pH under low supersaturation conditions. Typically, for the synthesis of interlayer carbonate hydrotalcite sample with a Mg/Al molar ratio 3, an mixed solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.045 mol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.015 mol) were made in 60 mL deionized water. Then the mixed solution (60 mL) containing  $\text{NaOH}$  (0.108 mol) and  $\text{Na}_2\text{CO}_3$  (0.0075 mol) were prepared. The two solutions were added slowly to a 250 mL flask under

vigorous stirring maintaining pH 10 at room temperature. The resulting slurry was aged for 24 h at 60 °C. The product was centrifuged and washed with deionized water 3~4 times. Finally, the colloidal solution of LDHs was diluted and injected into the flow injection system.

### **Synthesis of Mg-Al-NO<sub>3</sub> LDHs**

The Mg-Al-NO<sub>3</sub> LDHs was also synthesized by the co-precipitation method at constant pH under low supersaturation conditions. The preparation was performed under a nitrogen atmosphere to exclude the aqueous CO<sub>2</sub>. Solution A was mixed with 0.045 mol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.015 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 60 mL of degassed and deionized water. Solution B was mixed with 0.12 mol NaOH. The two solutions were added slowly to a 250 mL flask under vigorous stirring maintaining pH 10 at room temperature. The resulting white precipitate was aged for 24 h at 60 °C.

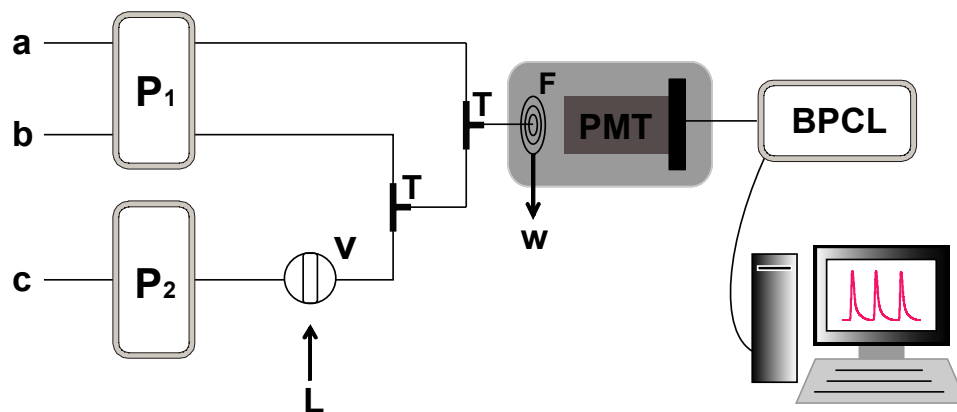
### **Apparatus**

The powder X-ray diffraction (XRD) measurements were performed on a Rigaku (Japan) D/max2500VB2+/PC X-ray diffractometer equipped with graphite-monochromatized Cu/K $\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ). The  $2\theta$  angle of the diffractometer was stepped from 5° to 70° at a scan rate of 0.02°/s. Hitachi (Japan) S-4700 field-emission scanning electron microscope (SEM) was used for obtaining the scanning electron microscopy images. The CL spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at a slit of 10 nm and at a scanning rate of 1200 nm/min. The excitation lamp was off and the emission slit width was opened maximally to 10 nm during the CL spectra recording. The CL detection was conducted on a BPCL luminescence analyzer (Institute of Biophysics, Chinese Academy of Science,

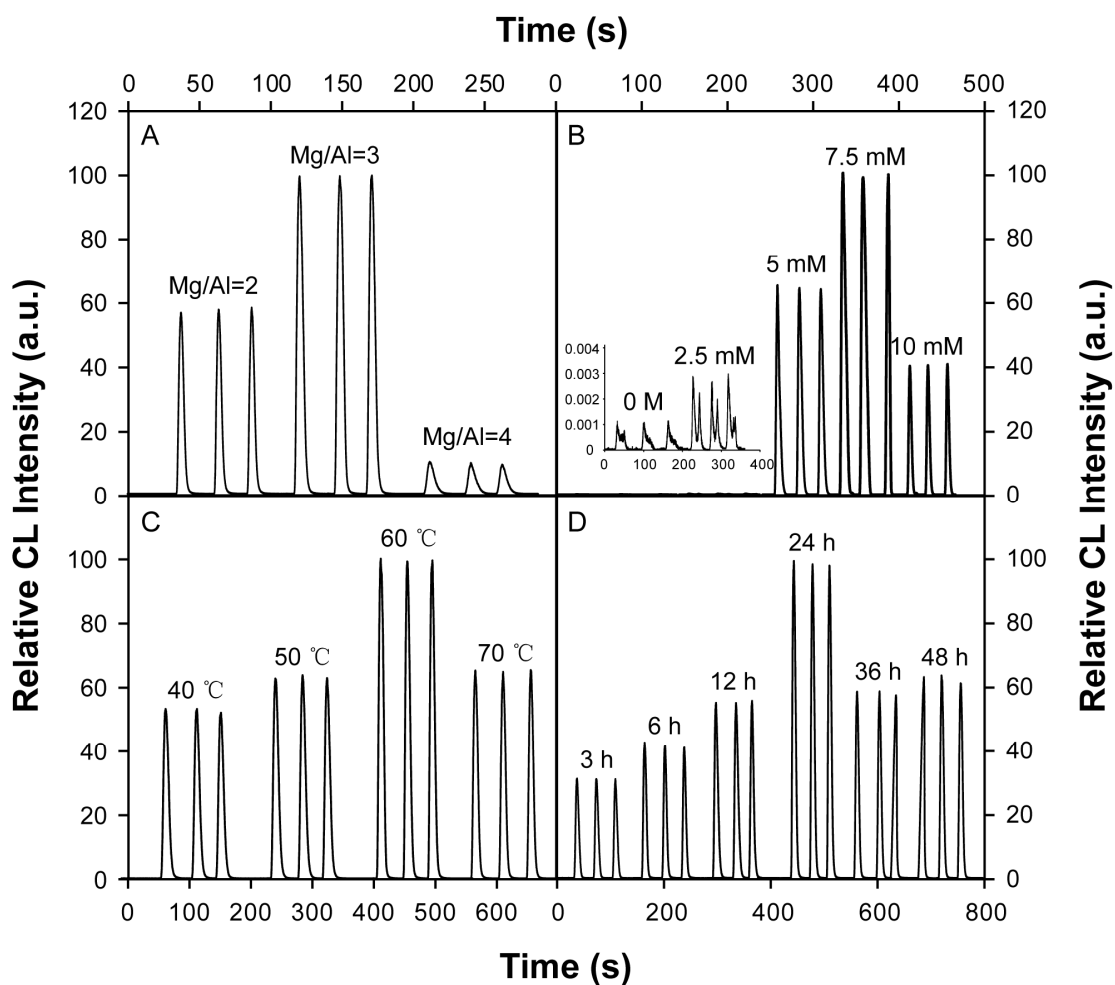
## CL Measurements

The schematic diagram of the flow system was shown in Fig. S1 in Supplementary Material. It consisted of two peristaltic pumps (BT-100M, Baoding, China), a 100  $\mu$ L loop injector, six-way injection valve (Shimadzu, Tokyo, Japan), a CL flow cell (PTEF: 30 cm in length and 0.5 mm i.d.), and a BPCL luminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). In order to investigate the effect of the LDHs crystal activity on the luminol-H<sub>2</sub>O<sub>2</sub> CL system, the as-prepared Mg-Al LDHs colloidal solution was injected into the carrier stream (deionized water) through a valve injector, which mixed with 0.2 mM luminol, and finally getting mixed with 1 mM H<sub>2</sub>O<sub>2</sub> solutions. The flow rate for the carrier stream, luminol or H<sub>2</sub>O<sub>2</sub> is 2.0 mL/min, separately. The CL signals were monitored by the PMT adjacent to the flow CL cell. The signal was imported to the computer for data acquisition.

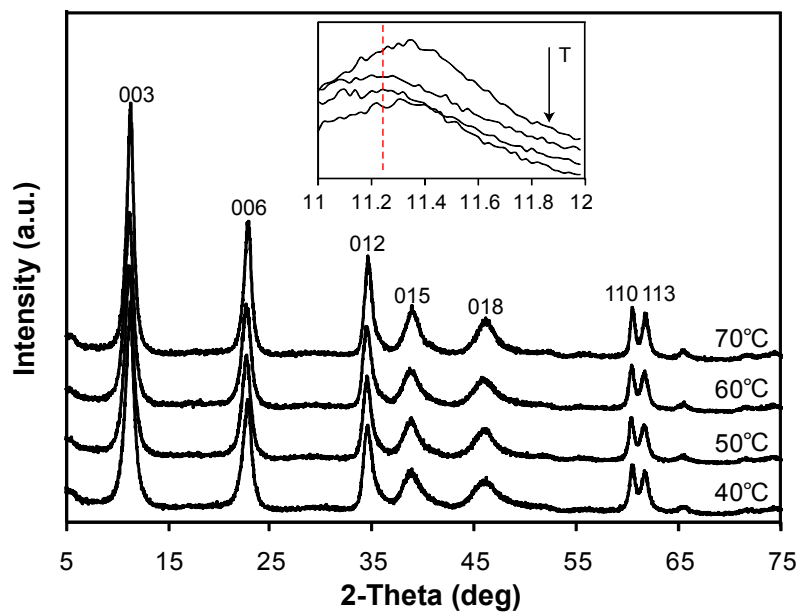
## Supporting Figures



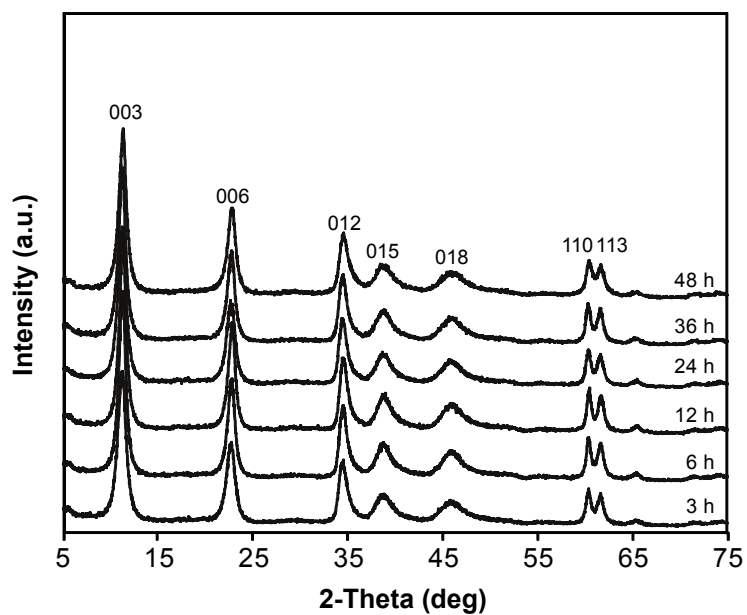
**Fig. S1** Schematic diagram of the flow injection CL detection system. a: H<sub>2</sub>O<sub>2</sub>; b: luminol; c: H<sub>2</sub>O; L: Mg-Al LDHs; v: six-way injection valve; T: three-way pieces; W: waste; P<sub>1</sub> and P<sub>2</sub>: peristaltic pumps; F: flow cell; PMT: photomultiplier tube.



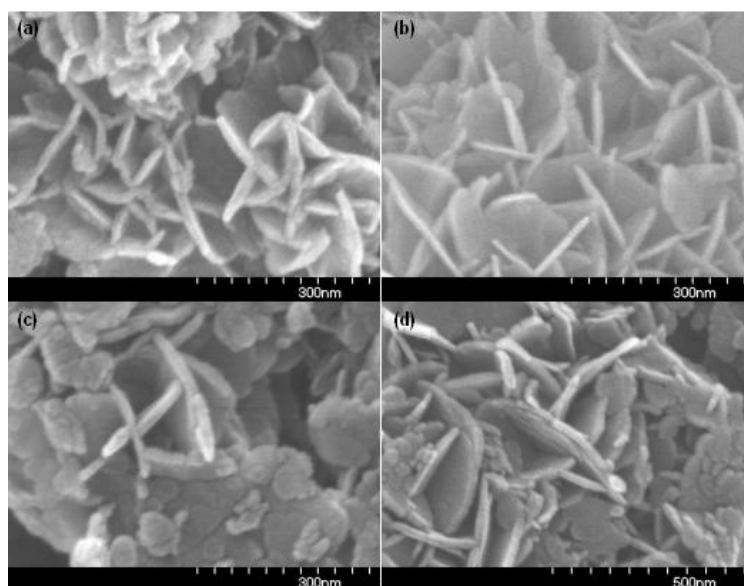
**Fig. S2** Effects of the Mg-Al-CO<sub>3</sub> LDHs synthesis conditions on the luminol-H<sub>2</sub>O<sub>2</sub> CL. (A) Effect of Mg to Al molar ratio; (B) Effect of the carbonate loading; (C) Effect of reaction temperature; (D) Effect of the reaction time. Experimental conditions are same as the CL measurements section.



**Fig. S3** Powder XRD patterns of Mg-Al CO<sub>3</sub> LDHs with different reaction temperatures.



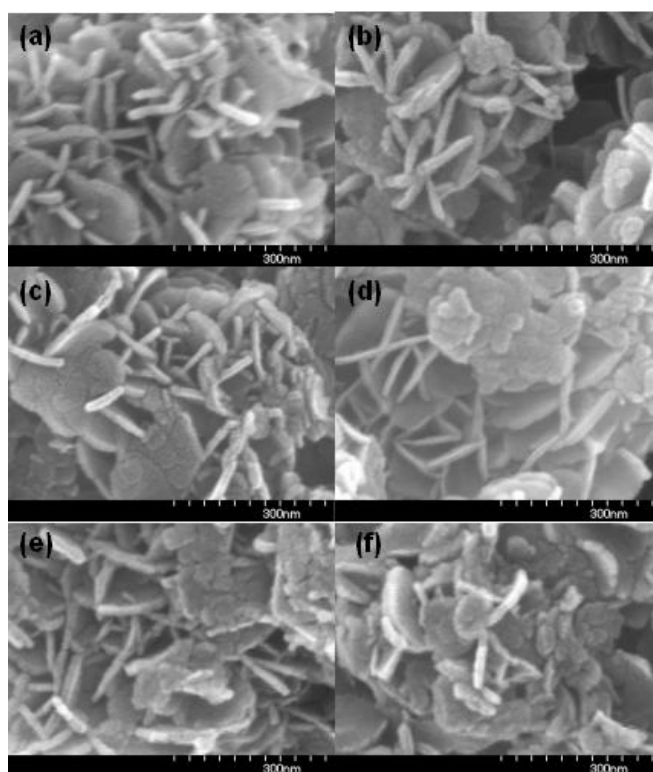
**Fig. S4** Powder XRD patterns of Mg-Al CO<sub>3</sub> LDHs with different reaction times.



**Fig. S5** SEM images of Mg-Al CO<sub>3</sub> LDHs with different reaction temperatures.

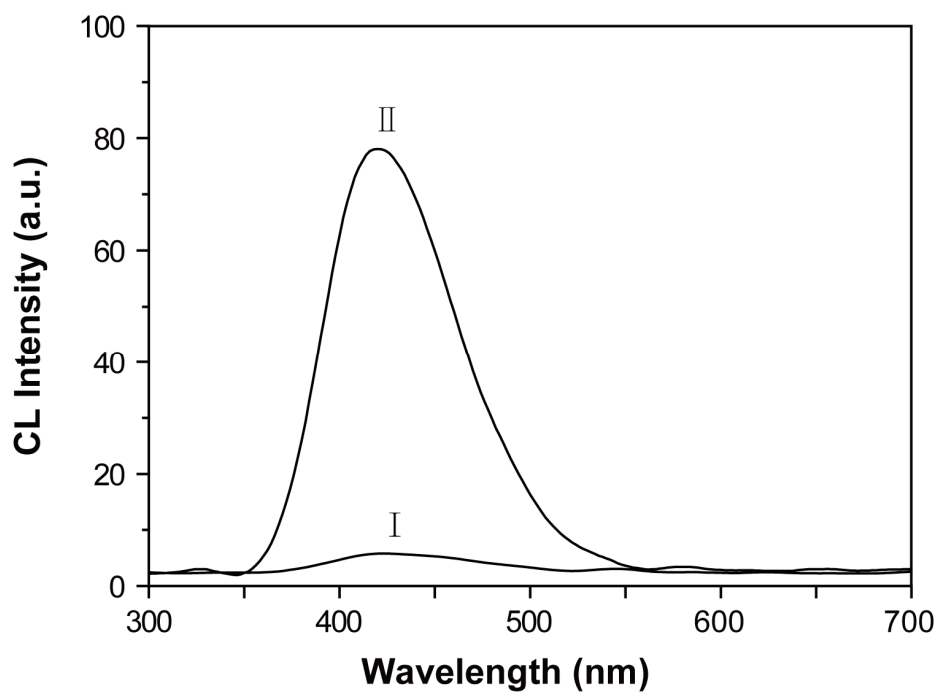
(a) 40 °C; (b) 50 °C; (c) 60 °C; (d) 70 °C



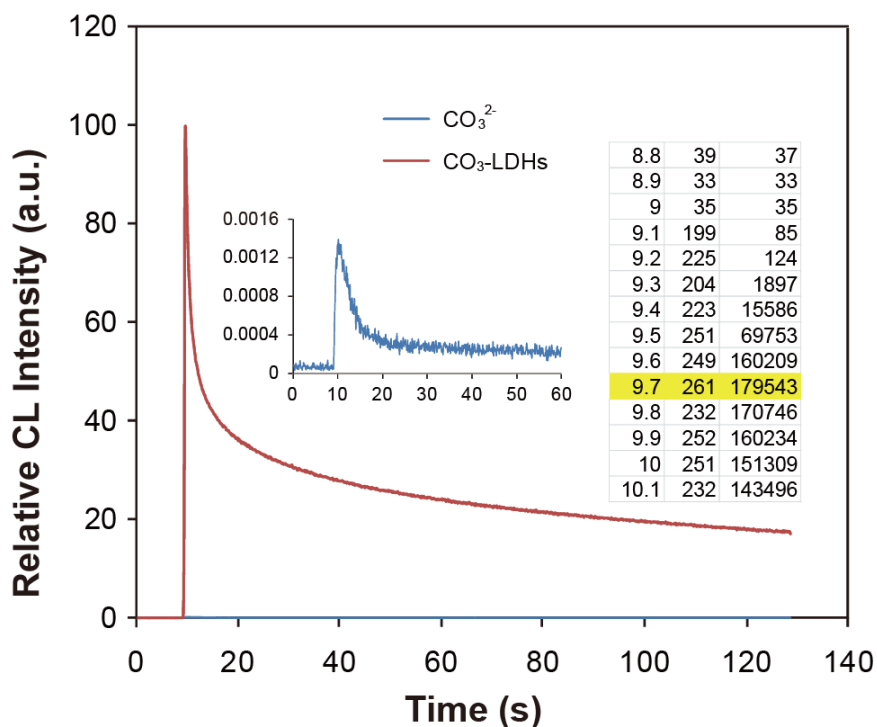


**Fig. S6** SEM images of Mg-Al CO<sub>3</sub> LDHs with different reaction times.

(a) 3 h; (b) 6 h; (c) 12 h; (d) 24 h; (e) 36h; (f) 48 h.

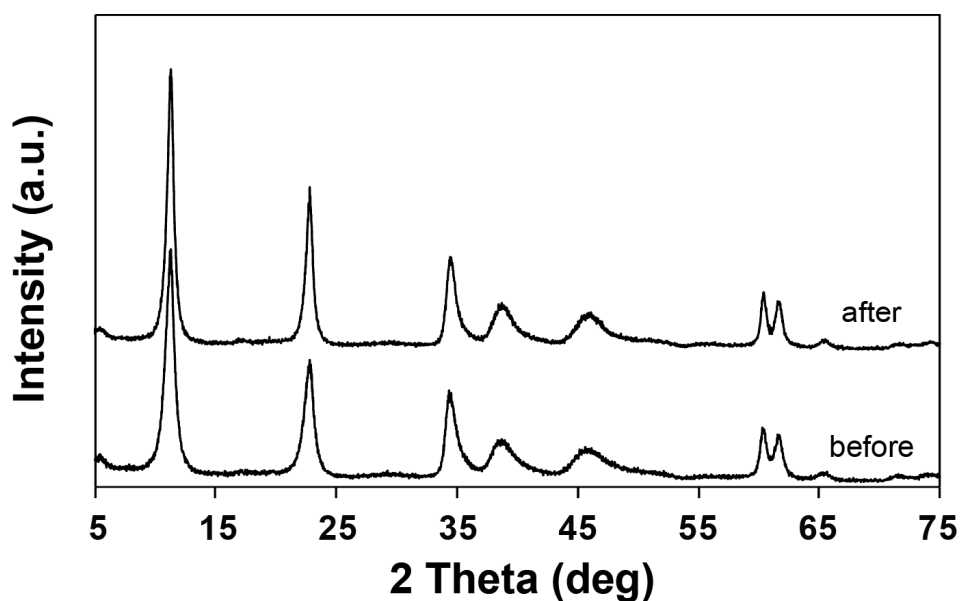


**Fig. S7** CL spectra for the luminol-H<sub>2</sub>O<sub>2</sub> system in the absence (I) and presence (II) of Mg-Al-CO<sub>3</sub> LDHs.



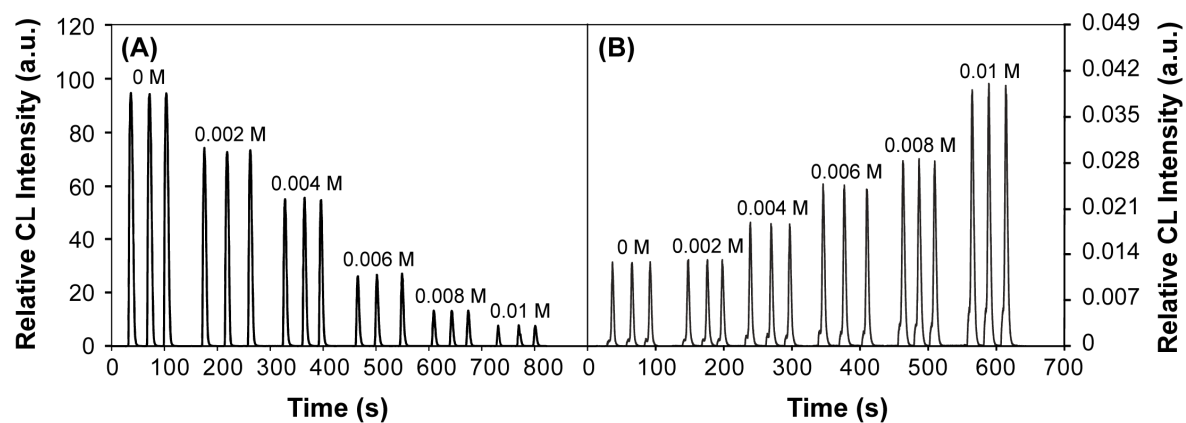
**Fig. S8** Kinetic CL intensity-time profile from luminol-H<sub>2</sub>O<sub>2</sub>-Mg-Al-CO<sub>3</sub> LDHs and luminol-H<sub>2</sub>O<sub>2</sub>-CO<sub>3</sub><sup>2-</sup>.

Experimental procedure: 150  $\mu$ L 0.2 mM luminol and 150 $\mu$ L 1 mM H<sub>2</sub>O<sub>2</sub> were respectively added to a reaction cuvette by an adjustable volume mechanical pipette, then 150  $\mu$ L the as-prepared Mg-Al-CO<sub>3</sub> LDH or 0.0625 M CO<sub>3</sub><sup>2-</sup> was injected via a microliter syringe through the upper injection port in a BPCL luminescence analyzer.

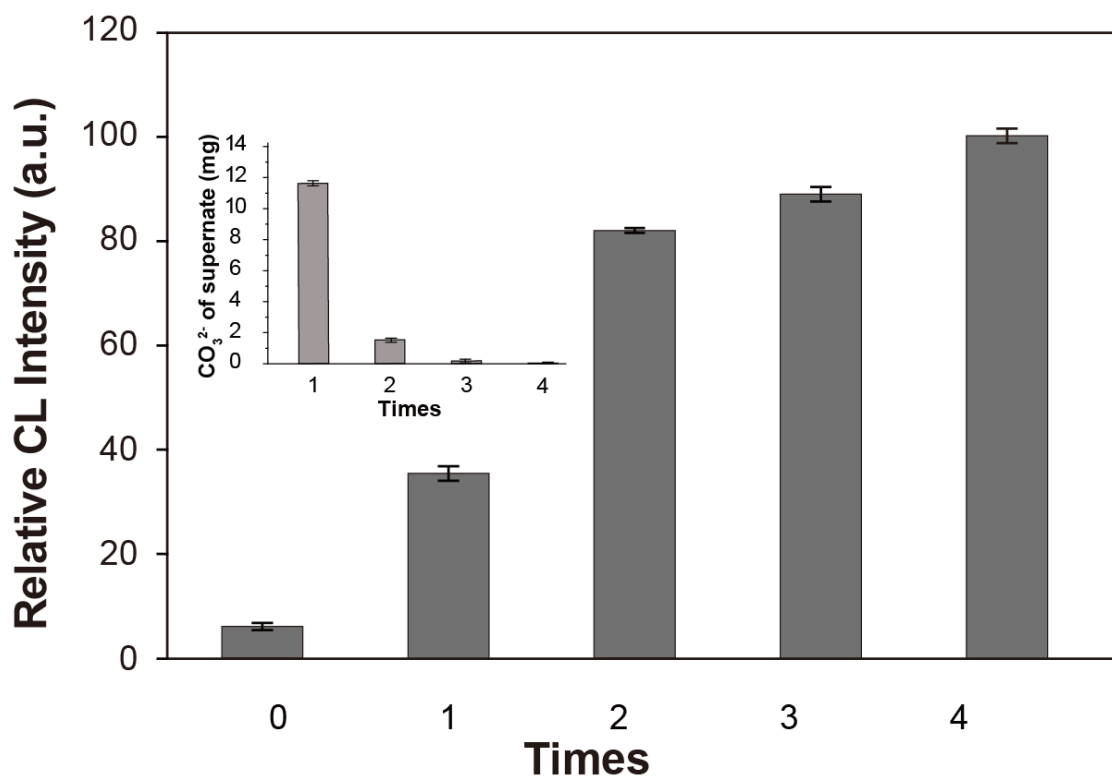


**Fig. S9** Powder XRD patterns of Mg-Al-CO<sub>3</sub> LDHs before and after the CL reaction.

Experimental procedure: 13 mg/mL Mg-Al-CO<sub>3</sub> LDHs, 1 mM H<sub>2</sub>O<sub>2</sub>, 0.2 mM luminol solutions were fed through separate lines into flow injection system. The mixture solution was obtained in outlet (W in Fig. S1), and was centrifuged at 4000 rpm for 10 min. The Mg-Al-CO<sub>3</sub> LDHs at the bottom was dried at 60 °C for 24 h. Finally, the XRD measurements were performed.



**Fig. S10** Different amount of carbonate in (A) Mg-Al-CO<sub>3</sub> LDHs and (B) Mg-Al-NO<sub>3</sub> LDHs.



**Fig. S11** CL intensity of Mg-Al-CO<sub>3</sub> LDHs and carbonate in the supernatant liquid after different centrifugation times.

Supplementary Material (ESI) for Chemical Communications

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Centrifugation procedure: 20 mL of the as-prepared Mg-Al-CO<sub>3</sub> LDHs was centrifuged at 4000 rpm for 10 min. The supernatant liquid was used for measuring carbonate content by gravimetric analysis. The Mg-Al-CO<sub>3</sub> LDHs at the bottom was diluted before injection into flow-injection CL system.