

Supporting information

**LDH/MgCO₃ hybrid multilayer on an aluminium substrate as a
novel high-temperature CO₂ adsorbent**

Yaqian Qiao,^a Junya Wang,^a Liang Huang,^a Qianwen Zheng,^a Dermot O'Hare,^b Qiang
Wang^{a,*}

^aCollege of Environmental Science and Engineering, Beijing Forestry University, 35
Qinghua East Road, Haidian District, Beijing 100083, China.

^bChemistry Research Laboratory, Department of Chemistry, University of Oxford,
Mansfield Road, Oxford, OX1 3TA, UK

Corresponding author:

College of Environmental Science and Engineering, Beijing Forestry University, 35
Qinghua East Road, Haidian District, Beijing 100083, China

E-mail: qiang.wang.ox@gmail.com, qiangwang@bjfu.edu.cn

Tel: +86-13699130626

1. Experimental details

1.1 Materials

The aluminium substrate (purity: > 99.0%; thickness: 0.1 mm) was purchased from Sinopharm Chemical Reagent Co., and the following analytical grade chemicals were also purchased from this company and used without further purification: ethanol, NaOH, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea. Deionized water was used in all the experimental processes.

1.2 Preparation of samples

Samples of multilayer MgAl-CO_3 LDH based thin film on an aluminium substrate was fabricated using a urea hydrolysis method. First, the aluminium substrate with a size of ca.100 mm X 100 mm was immersed in 0.5% aqueous NaOH solution (100 ml) for 5 min then was successively pretreated in deionized water and in ethanol each for 10 min respectively. At the same time, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea were dissolved in 100 ml deionized water. Typically, 0.0075 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.06 mol urea were mixed in 100 ml deionized water to form a solution (pH 6.7). The resulting solution was transferred to a 150 ml Teflon-lined stainless steel autoclave, and the as prepared Al substrate was placed vertically in the solution. The stainless steel autoclave was sealed put in a conventional oven at a fixed temperature (e.g. 90 °C) for different times. After crystallization, pH of the solution was between 6.9 and 7.7. The resulting film was rinsed with deionized water and ethanol, then dried under ambient conditions.

1.3 Characterization of samples

XRD patterns were recorded on a Shimadzu XRD-7100 instrument in reflection mode

with Cu K α radiation. The accelerating voltage was set at 40 kV with 30 mA current ($\lambda = 1.542 \text{ \AA}$). The reflection patterns were obtained in the range of 5–70° with a scanning rate of 5° s⁻¹. The morphology of samples was characterized using a scanning electron microscope (SEM, S-3400N II). The LDH/MgCO₃ hybrid multilayer on an aluminium substrate sample was directly placed on the stub. Before observation, the dried samples were sputtered and coated with gold for ~ 120 s under an argon atmosphere. The Langmuir specific surface areas (SSA) were measured from N₂ adsorption and desorption isotherms at 77 K collected from a Quadasorb SI physisorption analyzer (Micromeritics). Before each measurement, fresh and calcined samples were first degassed at 110 and 220 °C for 3 h.

1.4 Evaluation of CO₂ capture capacity

Thermogravimetric adsorption of CO₂ on the samples was measured using a Q50 TGA analyzer. Samples were first calcined at 400 °C for 5 h in N₂ (60 ml min⁻¹) before performing adsorption. To avoid the error caused by the memory effect, the test was carried out immediately after the first calcination. Usually, about 15 mg calcined sample was charged for the adsorption performance test. During CO₂ adsorption test progress, the samples were further calcined in situ at 400 °C for 1 h in N₂ (60 ml min⁻¹) before adsorption, and CO₂ adsorption experiments were carried out at 1 atm with a constant flow of CO₂ (20 ml min⁻¹) for 2 h. The regeneration and stability of the adsorbents were assessed by adsorption/desorption cycling tests. In the variable temperature test, the adsorption step was carried out at 200 °C for 30 min with a constant flow of CO₂ (20 ml min⁻¹), and the desorption was performed at 400 °C for 30 min with a constant flow of N₂ (60 ml min⁻¹). During the cycling, to ensure the accuracy of temperature control, we kept the targeted adsorption temperature for

40 min and protected with N₂ before switching to CO₂ for adsorption. For the CO₂ adsorption and desorption test, the sample synthesized with Mg/urea of 1:1, synthesis temperature of 140 °C, and synthesis time of 12 h, was used.

Table S1. The effect of Mg/urea ratio on the CO₂ capture capacity of the multilayer LDH thin film based adsorbents*.

Mg(NO ₃) ₂ (mol)	Urea (mol)	Mg(NO ₃) ₂ /urea (ratio)	CO ₂ capture capacity (mmol g ⁻¹)
0.0075	0.09	1:12	0.04
0.0075	0.075	1:10	0.12
0.0075	0.06	1: 8	0.18
0.0075	0.045	1: 6	0.11
0.0075	0.03	1: 4	0.17
0.005	0.06	1:12	0.18
0.015	0.06	1: 4	0.21
0.03	0.06	1: 2	0.24
0.06	0.06	1: 1	0.27
0.12	0.06	2: 1	0.25

*Synthesis temperature 140 °C, synthesis time 48 h, pH 6.5~6.9

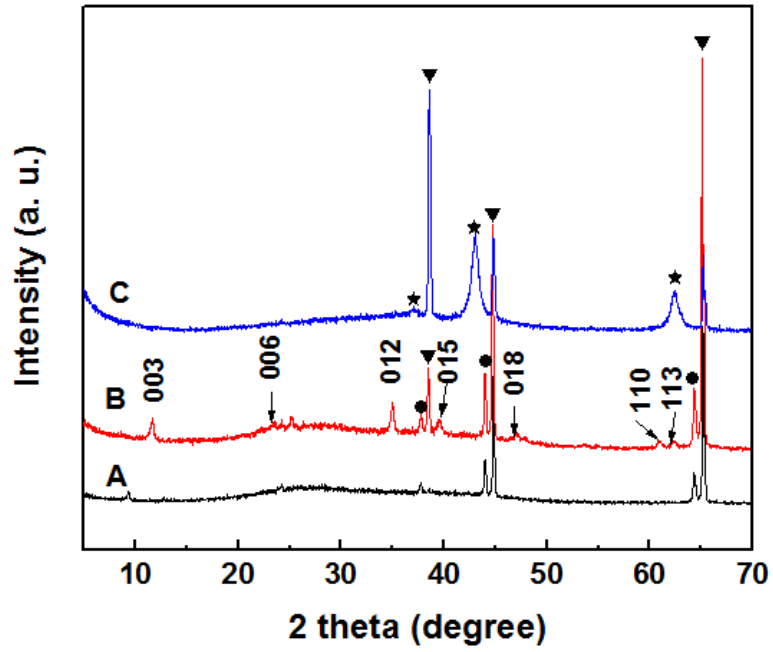


Figure S1. XRD diffraction patterns of Al substrate (A), the as-prepared MgAl-LDH precursor film (B), and calcined MgAl mixed metal oxide films powder (C). (▼) aluminium (JCPDS 85-1327), (●) aluminum hydroxide (JCPDS 70-2038), (★) MgO (JCPDS 71-1176).

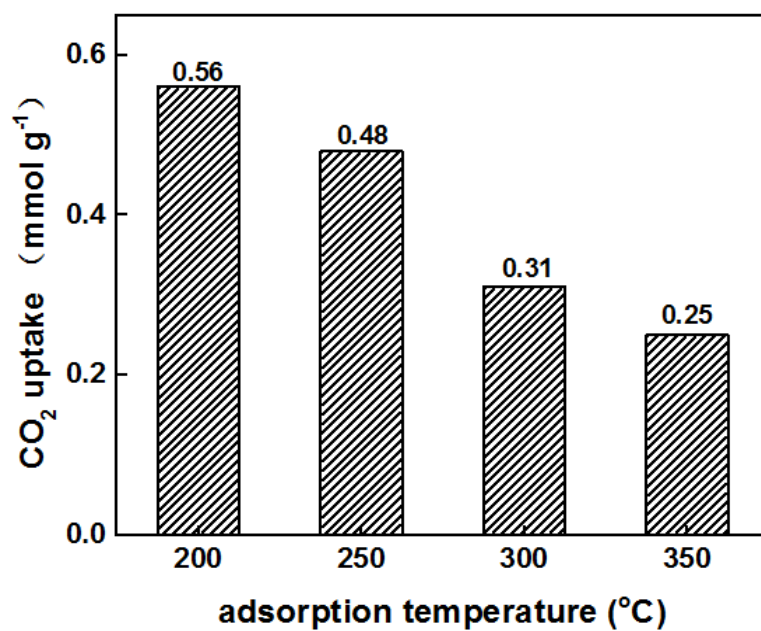


Figure S2. The effect of adsorption temperature on the CO₂ adsorption capacity of the LDH/MgCO₃ hybrid multilayer adsorbent (synthesis temperature 140 °C, synthesis time 12 h, and Mg/urea ratio=1:1).



Figure S3. The schematic diagram showing how the surface formed LDH and MgCO₃ films were separated by the Al-foil substrates.