

# Synthesis of layered double hydroxides/graphene oxide nanocomposite as a novel high-temperature CO<sub>2</sub> adsorbent

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## Abstract

In this contribution, a novel high-temperature CO<sub>2</sub> adsorbent consisting of Mg–Al layered double hydroxide (LDH) and graphene oxide (GO) nanosheets was prepared and evaluated. The nanocomposite-type adsorbent was synthesized based on the electrostatically driven self-assembly between positively charged Mg–Al LDH single sheet and negatively charged GO monolayer. The characteristics of this novel adsorbent were investigated using XRD, FE-SEM, HRTEM, FT-IR, BET and TGA. The results showed that both the CO<sub>2</sub> adsorption capacity and the multi-cycle stability of LDH were increased with the addition of GO owing to the enhanced particle dispersion and stabilization. In particular, the absolute CO<sub>2</sub> capture capacity of LDH was increased by more than twice by adding 6.54 wt% GO as support. GO appeared to be especially effective for supporting LDH sheets. Moreover, the CO<sub>2</sub> capture capacity of the adsorbent could be further increased by doping with 15 wt% K<sub>2</sub>CO<sub>3</sub>. This work demonstrated a new approach for the preparation of LDH-based hybrid-type adsorbents for CO<sub>2</sub> capture.

## Key words

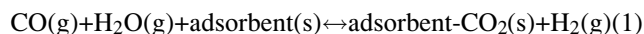
CO<sub>2</sub> capture; global warming; graphene oxide; hybrid materials; recycling

## 1. Introduction

Recently, there is a growing consensus that global climate change is occurring. As measured by Scripps Institute of Oceanography, CO<sub>2</sub> concentration was ca. 315 ppm in March 1958, which was increased to 391 ppm in January 2011, and to 398 ppm in January 2014 [1]. Now, it is widely accepted that the strong greenhouse gas effect significantly contributes to the global warming [2], which causes environmental problems like continuous rise of water-level in sea and the increasing number of ocean storms and floods, etc. [3]. Reducing the emission of CO<sub>2</sub> becomes the worldwide concerned problem, for which many techniques have been investigated, including substituting nuclear power for fossil fuels, increasing the efficiency of fossil plants, and capturing CO<sub>2</sub> prior to emission into the environment. All of these techniques have the attractive feature of limiting the amount of CO<sub>2</sub> emitted into

the atmosphere, but each has economic, technical, or societal limitations [4].

Sorption enhanced water gas shift (SEWGS) is well known as a promising pre-combustion CO<sub>2</sub> capture technology, which is a combination of WGS reaction and CO<sub>2</sub> sorption, as shown in Equation (1). Due to the existence of a solid CO<sub>2</sub> adsorbent, the produced CO<sub>2</sub> can be in situ captured. And in the meantime, the conversion of CO and the production of H<sub>2</sub> can be increased as well [5–8].



The key to ensure the success of this process is choosing a good CO<sub>2</sub> capturing material. Bearing in mind the limitations of the existing materials, there is an intense search for new adsorbents that exhibit good CO<sub>2</sub> adsorption capacity for SEWGS process. Layered double hydroxides (LDHs) are an

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interesting class of inorganic compounds, and in particular, their derivatives produced upon-calcination have desired properties as CO<sub>2</sub> adsorbents in pre-combustion capture applications [8–13].

For LDHs-derived CO<sub>2</sub> sorbents, starting from the natural mineral (Mg-Al-CO<sub>3</sub>), many works have been done. For instance, the effects of divalent cations [14], trivalent cations [15], charge compensating anions [13,16,17], Mg/Al ratio [18], synthesis method [19], the presence of SO<sub>2</sub> and H<sub>2</sub>O [9,20], particle size [21,22], alkali metal (K, Cs) doping [10,16,22–27], supported LDHs [28], and operational pressure [29] on CO<sub>2</sub> adsorption have all been reported. Except for changing the composition of LDHs, another effective way to improve the CO<sub>2</sub> capture capacities is to control the particle size of the LDHs. For the adsorbents, decreasing the particle size or improving the specific surface area then improves the surface adsorption activity site, which then improves the CO<sub>2</sub> capture capacities. Meis et al. [28] have studied the relationship between platelet sizes of LDHs and their CO<sub>2</sub> sorption capacities. The results showed that the LDHs with a platelet size between 30 nm and 2 μm have an invariant adsorption capacity (~0.1 mmol/g). However, the supported LDH samples with a platelet size of ~20 nm had much higher capacities. They proposed that the CO<sub>2</sub> sorption capacities of LDHs are determined by the amounts of low-coordination oxygen sites in Mg(Al)O<sub>x</sub> nanoparticles. Besides, Wang et al. [12] also found that the nano-sized spherical Mg<sub>3</sub>Al<sub>1</sub>-CO<sub>3</sub> LDHs with an average particle size of ca. 20 nm showed an increased CO<sub>2</sub> capture capacity. Recently, Garcia-Gallastegui et al. [30] synthesized a LDH/graphene oxide (GO) hybrid material by co-precipitation method for CO<sub>2</sub> capture, and they confirmed that both the CO<sub>2</sub> sorption capacity and recyclability were increased when LDHs were supported onto GO, which could be attributed to the enhanced particle dispersion.

It is believed that reducing the particle size of LDH can increase its CO<sub>2</sub> adsorption capacity. However, due to the layered feature of LDHs, it is difficult to further reduce the particle size lower than 20 nm. In this contribution, we report that the delamination of LDHs into single layer may be the most effective solution to this problem [31]. The delaminated nanosheets have an exceedingly high two-dimensionality with a molecular thickness, higher specific surface area, more degree of freedom, and more crystal orientation, etc. [31]. However, because of the strong surface charge density of LDHs monolayer [32], it is easy to restack and it is very difficult to separate the delaminated LDHs monolayer from solution. In order to tackle the restacking and separation issue, negatively charged graphene oxide single sheets are introduced to the exfoliated LDHs dispersion solution [33]. The electrostatic interaction between GO and LDHs creates a layered assembly of two sheets. The resulting nanocomposite contains exfoliated LDHs and GO nanosheets and its performance for CO<sub>2</sub> capture is reported for the first time. In principle, such assembly is beneficial for maximizing the dispersion of LDH nanosheets on the surface of GO, which can consequently increase the utilization rate of LDH as active CO<sub>2</sub> adsorption materials.

## 2. Experimental

### 2.1. Synthesis of samples

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

A salt solution (100 mL) containing a mixture of 0.075 mol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.025 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was added dropwise to a basic solution (100 mL) containing 0.05 mol Na<sub>2</sub>NO<sub>3</sub>. The pH value of the mixture solution was kept constant at 10 by the addition of a NaOH solution (3.4 mol/L). The resulting mixture was hydrothermally treated at 120 °C overnight. After hydrothermal aging, the sample was filtered and washed with deionized water until pH = 7, then dried at 100 °C in an oven. The obtained sample was Mg-Al-NO<sub>3</sub> LDHs.

#### 2.1.2. Synthesis of graphite oxide

Graphite oxide was prepared from the natural graphite power according to a modified Hummers method [34]. The graphitic oxide was prepared by stirring some powdered flake graphite and sodium nitrate into the concentrated H<sub>2</sub>SO<sub>4</sub>. Then KMnO<sub>4</sub> was added gradually with stirring while keeping the temperature of the mixture below 20 °C with ice-bath. The mixture was then stirred at 35 °C for 30 min, followed by the addition of some distilled water. After another 30 min stirring, some distilled water was then added to terminate the reaction. Subsequently, 30 wt% H<sub>2</sub>O<sub>2</sub> was added and the color of the mixture changed to bright yellow. The mixture was centrifuged and washed with 10 wt% HCl solution to remove the residual metal ions. The precipitate was then washed with Milli-Q water and centrifuged repeatedly until the solution became neutral, then dried at 100 °C in an oven. The obtained sample was graphite oxide.

#### 2.1.3. Delamination of LDHs

For the delamination of LDHs, 0.5 g Mg-Al-NO<sub>3</sub> LDHs were put into 50 mL formamide, followed by magnetic stirring till no sediment was observed upon standing. The concentration of delaminated Mg-Al-NO<sub>3</sub> LDHs dispersion was 10 g/L, which was marked Mg-Al-NO<sub>3</sub> LDH-NS.

#### 2.1.4. Delamination of graphite oxide

To delaminate graphite oxide, the product was treated with an ultrasonic probe at 700 W for 1 h, followed by centrifuging at 8000 rpm for 10 min. The delaminated graphite oxide was obtained in the supernatant. The precipitate was delaminated repeatedly. The concentration of delaminated graphite oxide dispersion, which was 1 g/L, was determined by drying 100 mL supernatant at 60 °C for two days, followed by measuring the mass using electronic balance.

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