



## Surface charging of layered double hydroxides during dynamic interactions of anions at the interfaces

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### ABSTRACT

In this research, we investigated the effect of dynamic anion adsorption/exchange on the surface charging property of Mg<sub>2</sub>Al–Cl–LDH and Mg<sub>2</sub>Al–CO<sub>3</sub>–LDH particles that show the average zeta potential of 41 and 34 mV in the as-prepared suspension, respectively. The addition of NaCl up to 3 × 10<sup>−3</sup> M in the suspension does not obviously affect the zeta potential of both LDHs, which can be attributed to the less affinity of Cl<sup>−</sup> to LDH. The introduction of Na<sub>2</sub>CO<sub>3</sub> severely reduces the zeta potential at the CO<sub>3</sub><sup>2−</sup> concentration higher than 1 × 10<sup>−4</sup> M, and to the negative value in both LDH systems at ca. 2 × 10<sup>−3</sup> M, which is presumably resulted from the exchange and the re-orientation of CO<sub>3</sub><sup>2−</sup> in a tilt/vertical style on the surface. All four organic anions (dodecyl sulfate, folate, citrate and polyacrylate) also significantly affect the zeta potential of the LDH particles. At the lower concentrations of organic anionic groups (<1 × 10<sup>−4</sup> M), the zeta potential was slightly affected, i.e. limited exchange/adsorption. However, the concentration increasing to some point suddenly decreases and reverses the zeta potential of the LDH particles, which is presumably caused by the hydrophobic interactions that bind the hydrophobic hydrocarbon chains (especially in dodecyl sulfate) into the micelle-like bilayer bunches on the LDH surface. In addition, the effect of pH in 5.5–11.0 on the LDH particle surface charging is mainly reflected through the conversion of CO<sub>3</sub><sup>2−</sup> to HCO<sub>3</sub><sup>−</sup>/H<sub>2</sub>CO<sub>3</sub> when pH decreases from ca. 11 to 6, with limited contribution from protonation/deprotonation and exchange/adsorption.

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### 1. Introduction

Inorganic nanoparticles have been emerged as new non-viral delivery agents only in the recent decade, and there are many inorganic materials, such as calcium phosphate, gold, carbon materials, silicon oxide, iron oxide and layered double hydroxides (LDHs), being extensively investigated [1]. This is due to recognition of their versatile features suitable for cellular delivery, such as wide availability, rich surface functionality, good biocompatibility, potential capability of target delivery and sustained release [1]. In particular, LDH has been paid more attention as efficient delivery vehicles of drug, nucleotides/genes, biomedical and other functional molecules [2–4].

LDH, also known as hydrotalcite-like material, can be found in nature as minerals and readily synthesized in the laboratory, with majority adhering to the general formula [M<sup>II</sup><sub>1−x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n−</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, where M<sup>II</sup> represents a divalent metal cation, M<sup>III</sup> a trivalent metal cation and A<sup>n−</sup> an anion. Struc-

turally, LDHs consist of cationic brucite-like layers and interlayer anions as well as water molecules. In the brucite-like layer [M<sup>II</sup>(OH)<sub>2</sub>], the partial substitution of M<sup>II</sup> by M<sup>III</sup> leads to a positive charge ([M<sup>II</sup><sub>1−x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>), which is neutralized by the interlayer exchangeable anion [(A<sup>n−</sup>)<sub>x/n</sub>] while various amounts of water (mH<sub>2</sub>O) are hydrogen bonded to the hydroxide layers and/or to the interlayer anions [5,6], forming the 3-D layered structure.

LDH particles prepared in the laboratory are normally hexagonal platelets, with the lateral sizes varying from 50 to 1000 nm and the aspect ratio in 5–10, while they are severely agglomerated into aggregates with the sizes up to 10 μm [7,8]. Recently, we developed a reliable method with which the LDH platelet dimension can be well controlled in 50–300 nm and these platelets can be homogeneously dispersed in the aqueous suspension [8]. Therefore, if the LDH platelet dimension is controlled under 150–200 nm, the cellular delivery of such LDH platelets should be efficient [9]. However, when we further carried out the delivery of supercoiled pEF-eGFP plasmid (ca. 6.1 kbp) to various cell lines using these LDH particles, we noted that the delivery efficiency was rather low in comparison with the polymeric delivery vehicle [10]. Many other papers reported the successful delivery of various gene segments

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[3,11–13], but the efficiency was much lower than the commercial polymeric agents [1,3,10,13]. The low delivery efficiency, in our belief, is due to aggregation of LDH–DNA hybrid particles into large aggregates during preparing the LDH–DNA nanohybrid suspension and mixing it to the culture medium.

It is well known that dispersion and aggregation of any particles in the suspension are related to their zeta potential [14]. Because inorgano-LDH particles normally have a zeta potential of 30–50 mV, they can be well dispersed in the suspension with the suitable methods, such as hydrothermal treatment [15]. However, this high positive zeta potential is reduced when the particles are interacting with gene segments, or with organic/inorganic salts in solution, which could finally lead to agglomeration and sedimentation. Therefore, in this research, we dynamically investigated the surface charging of fully dispersed LDH particles in aqueous suspension when the organic/inorganic anions at various concentrations are interacting on the particle surface in order that we understand the surface charging and agglomeration of LDH particles in the salt solution, such as phosphate buffer saline solution.

## 2. Experimental

### 2.1. Preparation of LDH materials

Mg<sub>2</sub>Al–Cl–LDH and Mg<sub>2</sub>Al–CO<sub>3</sub>–LDH particle suspensions were prepared with a quick precipitation and subsequent hydrothermal treatment [8,15]. In brief, 3.0 mmol of MgCl<sub>2</sub>·6H<sub>2</sub>O (>98%, Aldrich) and 1.0 mmol of AlCl<sub>3</sub>·6H<sub>2</sub>O (>98%, Aldrich) were dissolved in 10 mL deionized water. This salt solution was then rapidly added to a basic solution (40 mL) containing 6.0 mmol of NaOH (>97%, Ajax Finechem) within 5 s to generate the precipitate of Mg<sub>2</sub>Al–Cl–LDH. After stirring for 10 min in N<sub>2</sub> stream at room temperature, the precipitate was collected via centrifugation and further washed twice. Henceforth, the washed precipitate was manually dispersed in 40 mL of deionized water and placed in a 45 mL autoclave with Teflon linen, followed by hydrothermal treatment at 100 °C in an oven for 16 h to give the suspension of Mg<sub>2</sub>Al–Cl–LDH particles (regarded as ‘salt-free’ suspension).

Similarly, 2.0 mmol of MgCl<sub>2</sub>·6H<sub>2</sub>O and 1.0 mmol of AlCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 10 mL deionized water, which was then rapidly added to a basic solution (40 mL) containing 6.0 mmol of NaOH and 0.6 mmol of Na<sub>2</sub>CO<sub>3</sub> (>99%, Ajax Finechem) within 5 s to generate the precipitate of Mg<sub>2</sub>Al–CO<sub>3</sub>–LDH and stirred for 10 min at room temperature. The stirred mixture was post-treated in the same way as above to generate the suspension of Mg<sub>2</sub>Al–CO<sub>3</sub>–LDH particles.

### 2.2. Materials characterization

Mg<sub>2</sub>Al–Cl–LDH and Mg<sub>2</sub>Al–CO<sub>3</sub>–LDH materials were identified by X-ray powder diffraction (XRD), using a Bruker D8 Advance Research X-ray diffractometer with copper K<sub>α</sub> radiation ( $\lambda = 0.15418$  nm) at a scanning rate of 1.2°/min over a  $2\theta$  range of 8°–65°. The LDH samples were mounted on glass slides in the thin film form by dropping a few drops of the as-prepared LDH particle suspension. The instrument was calibrated with the crystalline silicon and the basal spacing was determined from the characteristic diffraction peaks. Fourier transform infrared (FTIR) spectra were acquired over the range of 4000–400 cm<sup>-1</sup> with 40 scans at a resolution of 4.0 cm<sup>-1</sup> on a Nicolet 6700 FTIR by measuring the KBr pellet containing 1–2 wt% of the LDH sample.

Photon correlation spectroscopy (PCS, Nanosizer Nano ZS, Malvern Instruments) was used to analyze the particle size distribution of the LDH suspensions from 0.6 to 6000 nm at 25 °C, in which the peak position was automatically calculated. The water refractive index (RI) of 1.33 and the water viscosity of 0.8872 cP

were employed while the RI of LDH materials was arbitrarily assigned 1.55.

The transmission electron microscopic (TEM) images were recorded on a JEOL JSM-2010 transmission electron microscope (TEM) at an acceleration voltage of 200 kV. For TEM imaging, a droplet of the diluted as-prepared LDH particle suspension (1:10) was dropped on a copper grid coated with the holey carbon film.

### 2.3. Zeta potential monitoring during titrations

Zeta potentials of the two diluted LDH suspensions were also measured using the Zetasizer Nano ZS (Malvern Instruments) with the water RI of 1.33, the water dielectric constant of 78.55 and the water viscosity of 0.8872 cP. In order to dynamically monitor the change of the zeta potential when an organic/inorganic salt or acid/base solution was continuously mixed with the LDH suspension, the measurement was performed using the MPT-2 Autotitrator associated to Zetasizer Nano ZS where the titration system was well sealed. In the first step, each LDH suspension of 1.0 mL was diluted with 9.0 mL of deionized water in a 25 mL sample container which was then attached to the MPT-2 Autotitrator. The diluted LDH suspension was kept at 25 °C and started to circulate into the zeta cell. The zeta potential was monitored and became stabilized after circulation for 3–5 min. After stabilization, the zeta potential was read by accumulating 30 times, which was regarded as the zeta potential of the as-prepared LDH particles.

In the next step, the diluted LDH suspension was injected with dilute NaOH solution (0.01 M) to adjust pH of the LDH suspension (ca. 9.0) to ca. 11.0 via the autotitration set-up. The zeta potential and the exact pH were read after the reading was stabilized. To monitor the zeta potential changing with pH, the dilute HCl (0.01 M) was automatically injected to the LDH suspension to change pH to a pre-designed value in the range from 11.0 to 5.5. After injection, the suspension was circulated, and zeta potential was measured only after the zeta potential reading became stable. Then the injection of dilute HCl solution was repeated to the next pH until to 5.5. The reverse autotitration from pH 5.5 to 11.0 was continued with injecting dilute NaOH solution in the similar way, with recording the zeta potential at each pH.

Alternatively, an inorganic/organic salt solution was injected to the diluted LDH suspension to investigate the dynamic exchange/adsorption of the inorganic/organic anion on the LDH particle surface at 25 °C through monitoring the zeta potential change. For example, dilute NaCl (0.01 M) or Na<sub>2</sub>CO<sub>3</sub> (0.01 M) solution was added to the LDH suspension with [Cl<sup>-</sup>] or [CO<sub>3</sub><sup>2-</sup>] varying from 1.0 × 10<sup>-5</sup> to 3.0 × 10<sup>-3</sup> M. At each pre-designed concentration point, the LDH suspension was circulated until the zeta potential reading was stable. In comparison, some organic anions were selected, including dodecyl sulfate (singly charged), folate (doubly charge), citrate (triply charged) and poly(acrylate) (multiply charged, MW = ~10,000). Their sodium salt solutions were made and auto-titrated to increase the anionic group (functionality: COO<sup>-</sup> or R–OSO<sub>3</sub><sup>-</sup>) concentration from 1.0–3.0 × 10<sup>-5</sup> to 3.0–9.0 × 10<sup>-3</sup> M, while the zeta potential at each point was monitored.

## 3. Results

### 3.1. Physicochemical features of LDH particles

Two as-prepared LDH suspensions look homogeneous and very transparent, with the LDH crystallite particles being well suspended in solution. As shown in Fig. 1, there is one distribution band for each LDH suspension. For instance, Mg<sub>2</sub>Al–Cl–LDH particles have the hydrodynamic diameters exclusively in 30–250 nm

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