



# Aerosol-assisted self-assembly of hybrid Layered Double Hydroxide particles into spherical architectures

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## ABSTRACT

Acetate intercalated NiAl-Layered Double Hydroxide nanoparticles were prepared by polyol process and further used as building blocks to form hybrid LDH spheres by a spray drying technique. The spherical aggregated LDH particles display a polydispersed size with a diameter ranging from 47 nm to 2 μm. The analysis of the thermal behavior evidenced that the spherical form was maintained upon calcination up to 1100 °C, giving rise to derived mixed oxide (NiO + NiAl<sub>2</sub>O<sub>4</sub>) nanospheres. Interestingly, the spherical morphology of the LDH materials was also retained during anion exchange process. The replacement of the intercalated acetate anion by of a voluminous anion such as dodecylsulfate induces an increase of the nanosphere mean diameter of 65%. The different materials were deeply characterized using X-ray diffraction, FTIR spectroscopy, scanning and transmission electron microscopies, dynamic light scattering, thermal analysis and nitrogen sorption.

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## 1. Introduction

Layered Double Hydroxides (LDH) represent an interesting class of 2D materials [1], which can be described by the general formula  $[M_{1-x}^{II}M_x^{III}(\text{OH})_2] [A_{x/m}^{m-} \cdot n\text{H}_2\text{O}]$ . The composition versatility of both the layer and the interlayer domain makes them useful in many fields of research such as (bio)-catalysis [2], environmental remediation processes [3], (bio)-nanocomposites [4] or for storage and control release of biomolecules [5] and drugs [6]. Because it is now well-established that particle size, shape and morphology strongly influence the physical and chemical properties of the materials, many works have been reported on the preparation of LDH and the control of their crystal structure, particle size, assembly and morphology [7]. The spherical shape is particularly desirable for specific applications for instance in medicine or nanocomposite science. Various synthetic strategies mainly based on the use of organic medium, surfactants or hard template, have been developed to access nanostructured LDH. Belt-like LDH structure was obtained in reverse microemulsion medium (dodecyl sulfate, water and isoctane) with subsequent modifications by nonionic triblock copolymer surfactant addition [8]. Gunawan

and Xu reported [9] that unusual coral like LDH microspheres can be formed in a nonaqueous system of ethylene glycol, methanol and dodecyl sulfate under solvothermal conditions. Surfactant molecules [10] such as dodecyl sulfate and dodecanesulfonate as well as biopolymer [11] appeared also as efficient morphology controlling agents under hydrothermal conditions. The latter have been reported to induce the formation of curved LDH layers aggregated in spherical forms. Another reported synthetic strategy lead to the use of glycine into the reaction medium as metal complexing agent [12]. Further thermolysis of complexes induces the LDH coprecipitation displaying original flower like morphologies.

In parallel, template syntheses [13] were also described to allow the formation of nanostructured LDH. For instance, LDH hollow nanospheres were successfully prepared by either layer by layer deposition of exfoliated LDH nanosheets at the surface of polystyrene beads [14] or direct assembly of LDH nanoparticles on carbon nanospheres [15]. Moreover, using an inverse opal templating method three dimensionally ordered macroporous LDH can be obtained [16,17]. It should be underlined that, easy processing techniques such as electrophoretic deposition, sonication and spray-drying have also been reported to produce LDH microspheres, without the use of any soft or hard template [18,19].

Amongst these latter, the spray drying also called aerosol method appears particularly as an attractive particle engineering technology widely used in various industries (food, pharmaceutical, ceramic, polymers...) to obtain dry particles from liquid feedstocks

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[20]. Thanks to the self-assembly into spherical confined droplets during fast drying, spherical particles of various materials such as silica, alumina, laponite have already been prepared [21]. It is noteworthy that aerosol process can be combined with evaporation induced self assembly (EISA) mechanism to produce spherical mesoporous materials [22] (silica, transition-metal oxides, organotalc. . .).

Herein, we report a spherical self-assembly of hybrid LDH nanoparticles based on the spray drying of a colloidal suspension of acetate intercalated LDH particles obtained by the polyol method [23]. The process uses hybrid LDH particles as building blocks in a bottom-up approach and permits to easily produce submicrometer hybrid LDH spherical particles.

## 2. Experimental section

### 2.1. Preparation of the samples

All chemicals were of analytical grade and used without any further purification. Deionised water and 95% ethanol were used in the synthesis and washing processes.

The starting LDH nanoparticles were prepared following the polyol method as previously described [23]. In a typical experiment,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Al}(\text{CH}_3\text{COO})_2(\text{OH})$ , (total concentration of salts of  $0.1 \text{ mol L}^{-1}$  and  $\text{M}^{2+}/\text{Al}^{3+} = 2$ ) are dispersed in 50 mL of ethylene glycol (EG). The suspension was heated at  $90^\circ\text{C}$  under stirring. After one hour, hydrolysis is performed by rapid addition of 22.5 mL of water. The suspension is further stirred under heating for 12 h. After this period, the solution was slowly cooled down at room temperature and centrifuged. The recovered gel was washed twice with ethanol. Then, 400 mL of a 1.2 g/L NiAl-Ac colloidal suspension was prepared by dispersing 8 g of gel (5.3% w/w) in ethanol.

As a reference sample, one part of the NiAl-Ac gel was air-dried.

### 2.2. Spray-drying treatment

The colloidal solution was then fed into the spray drying apparatus which is composed of a constant output atomizer (TSI model 3076), nominally providing droplet particles of 2000 nm mean diameter, at a fixed  $\text{N}_2$  gas pressure of 2 bars. The NiAl-Ac colloidal solution was pumped-out and sprayed-out of the atomizer in the form of fine particles that were then carried by the  $\text{N}_2$  gas flux to a tubular furnace operating at  $150^\circ\text{C}$  allowing the evaporation of water. Dried particles were collected on a 200 nm membrane filter. The spray-drying set-up is also composed with a vacuum flask refrigerated with an ice-bath to condense water and a vacuum pump to keep the gas flux constant in a laminar regime.

### 2.3. Characterization

Chemical analyses (Ni, Al, S, C, H) were performed at the Vernaison Analysis Center of CNRS. Ion chromatography was performed on a Dionex DX-320. Acetate anions were separated on an AS11 column. Powder X-ray diffraction (PXRD) patterns were obtained with a Siemens D501 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5415 \text{ \AA}$ ) and fitted with a graphite back-end monochromator. The samples were scanned from  $2^\circ$  to  $70^\circ$  ( $2\theta$ ) using steps of  $0.08^\circ$  and a counting time of 4 s per step. In-situ temperature XRD measurements were recorded by a Philips Model X'Pert Pro diffractometer ( $\text{Cu K}\alpha$ ) equipped with an Anton Paar Model HTK 16 chamber and RTMS detector. Scans were recorded in air atmosphere with the temperature ranging from  $25$ – $1100^\circ\text{C}$  with a heating rate of  $5^\circ\text{C}/\text{min}$  and an equilibration time of 15 min before measurement at each temperature. The measurement

conditions were in the range  $3$ – $70^\circ$  in continuous mode in step of 0.0334 with a count time of 200 s.

Attenuated Total Reflectance Fourier Transform Infrared (FT-IR) spectra were measured in the range  $400$ – $4000 \text{ cm}^{-1}$  on a FTIR Nicolet 5700 spectrometer (Thermo Electron Corporation) equipped with a Smart Orbit accessory. Dynamic light scattering (DLS) measurements were performed using a Malvern Instruments ZetaSiser Nano ZS equipped with a He-Ne laser ( $\lambda = 633 \text{ nm}$ ). Measurements, repeated three times for each sample, were made on as-made initial suspensions and spray-dried powder spread out in distilled water at a 5 g/L concentration.

SEM characteristics of the samples were performed on a Zeiss Supra 55 FEG-VP Field-Emission Scanning Electron Microscope (FE-SEM) operating at 3 kV. Specimens were mounted on conductive carbon adhesive tabs and imaged after carbon sputter coating to make them conductive. Transmission Electron Microscopy (TEM) images were observed with a Hitachi H-7650 transmission electron microscope (Hitachi, Elexience, France) at an acceleration voltage of 80 kV and photographed with a CCD AMT HR camera (Hamamatsu,  $1024 \times 1024$  pixels). Powders were dispersed in ethanol and then one droplet of the suspension was applied to a 400 Mesh holey carbon-coated copper grid and left to dry in air. Ultrathin sections (70 nm) prepared from material embedded in an epoxy resin were made with an ultramicrotome (UC6, Leica, France), mounted onto copper grids. Nitrogen adsorption-desorption analyses were performed at  $-196^\circ\text{C}$  with a Micromeritics ASAP 2020. Before analysis, samples were pretreated at  $120^\circ\text{C}$  under vacuum for 12 h. The surface areas were estimated by using the Brunauer-Emmett-Teller (BET) method. The BET surface areas were determined for the low-pressure region ( $0.05 < p/p_0 \leq 0.3$ ).

Thermogravimetric analyses (TGA) were recorded on a Setaram TG-DTA92 thermogravimetric analyser in the temperature range of  $25$ – $1050^\circ\text{C}$ , with a heating rate of  $5^\circ\text{C}/\text{min}$ , under an air flow in an alumina crucible.

## 3. Results and discussion

NiAl LDH phase was firstly prepared by hydrolysis of acetate precursors according to the polyol method as previously described [23]. This process carried out in polyol medium presents the interest to limit the crystal growth of the particles compared with the conventional coprecipitation. NiAl LDH compound is obtained in a gel form, which can be easily dispersed in solution leading to stable colloidal suspension of nanoparticles. The XRD pattern (Fig. 1A) of the air-dried gel exhibits typical feature of pure LDH structure with a series of 001 diffraction lines, characteristic of a layered structure.

The d-spacing of 1.25 nm traduces the presence of acetate anions in the interlayer domain, which is further confirmed by the observation of the asymmetric and symmetric carboxylate vibration bands of acetate respectively at  $1562$  and  $1422 \text{ cm}^{-1}$  on the IR spectra (Fig. 1B). A FE-SEM image of air-dried NiAl-Ac particles is shown in Fig. 2a. Individual particles cannot be distinguished as often observed for hybrid LDH and their aggregation leads to an ill-defined morphology. However, TEM image of a 1.2 g/L NiAl-Ac colloidal suspension (Fig. 2b) clearly evidences the formation of LDH platelets in the range of  $30$ – $100 \text{ nm}$ , appearing as needles when they are perpendicular to the Cu grid. Note that all our attempts to measure the starting NiAl-Ac particles size in solution by dynamic light scattering (DLS) were unsuccessful probably because of the gel-like structure.

After spray-drying of LDH suspension, the sample was characterized by FE-SEM. Fig. 3 shows typical images of the spray-dried NiAl-Ac sample. The morphology appears completely different compared to the air-dried sample previously described.

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