Volume 6
Number 8
21 April 2025
Pages 2451–2704

Materials Advances

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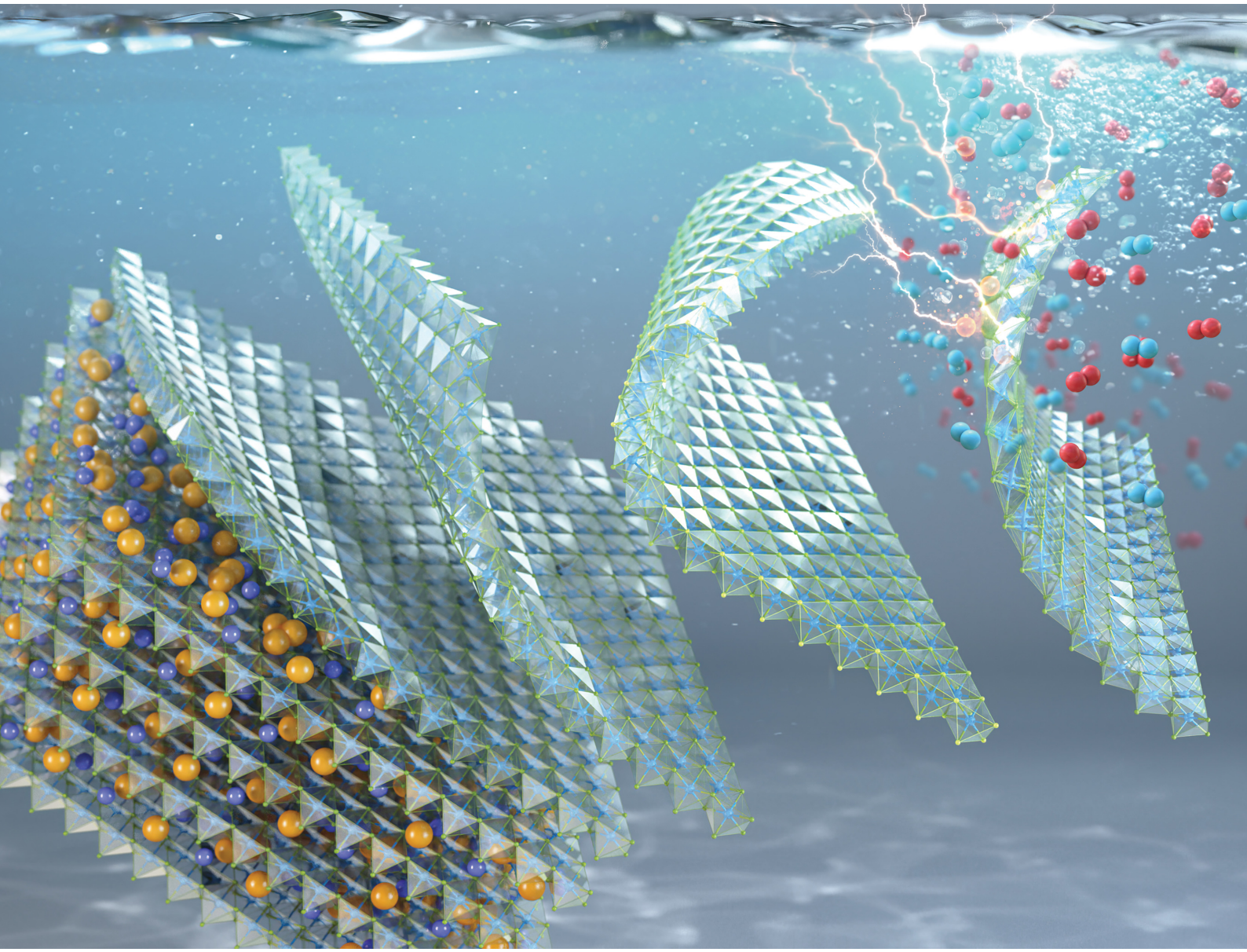

ISSN 2633-5409

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Cite this: *Mater. Adv.*, 2025, **6**, 2503

Received 14th January 2025,
Accepted 10th March 2025

DOI: 10.1039/d5ma00035a

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Alkali-free single-step synthesis of delaminated layered double hydroxides in water *via* an amino acid-assisted hydrothermal method†

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An alkali-free single step synthesis of delaminated CoAl layered double hydroxide was successfully performed in an aqueous medium using an amino acid-assisted hydrothermal reaction. The nanosheets obtained were highly stable after functionalization with amino acids.

Layered double hydroxides (LDHs) comprise positively charged nanosheets intercalated with anions and water. LDHs are used in almost all fields of chemistry. The delamination of LDH into nanosheets is an interesting method to obtain thin, positively charged two-dimensional nanosheets. Delaminated LDH nanosheets are widely used as catalysts,[1] as sorbents,[2] in magnetic and electrochemical applications,[3] *etc.* The delamination of LDHs into nanosheets is challenging because it requires the energy to overcome the electrostatic interactions between the metal hydroxides and interlayer anions. Delamination of LDHs was believed to be impossible until the pioneering work of Adachi Pagano *et al.*, who prepared delaminated LDH using a surfactant (dodecyl sulfate; DDS)-intercalated LDH in butanol.[4] Several methods have been developed for the delamination of LDHs, such as DDS intercalated LDH in acryl monomers under high shear,[5] amino acid-intercalated and nitrate-containing LDHs in formamide,[6] and microemulsion techniques.[7] The delamination of LDHs was largely performed in hazardous organic solvents such as formamide and DMSO. However, delamination in aqueous media can expand its use in advanced applications and thus demands a facile preparation method. An increase in the attention paid to LDH nanosheets for advanced applications, such as oxygen evolution catalysts,[1c] and precursors for nanostructured hybrid materials,[8] has led researchers to design facile preparation methods for such nanosheets. Few reports have been published on the possibility of LDH delamination in aqueous media. Hibino *et al.* first reported the delamination of lactate-intercalated LDH in a water medium.[9] Subsequently, the synthesis of stable colloidal suspensions of LDH in water has been explored *via* a hydrothermal method using inorganic anions containing LDHs prepared *via* co-precipitation and hexamine hydrolysis methods.[10] Further, delamination of acetate-intercalated LDH in water and exfoliation of LDH using aqueous NaOH/urea solution have been demonstrated.[11] However, these methods require multiple steps for the synthesis of delaminated LDH. For the first time, Yu *et al.* synthesized direct one-step LDH nanosheets *via* a bottom-up approach using formamide as a growth inhibitor.[12]

Biomolecules such as amino acids have recently been used to synthesize metal oxides and hydroxides. The formation of metal oxides, such as SnO_2 and ZrO_2, *via* lysine-mediated hydrolysis has been reported.[13] Moreover, metal hydroxides such as urchin-like $Co(OH)_2$ nanowires and thin α-$Co(OH)_2$ mesocrystal nanosheets have also been prepared using lysine and arginine-mediated hydrolysis methods, respectively.[14] Apart from the synthesis of metal oxide/hydroxide, amino acids have also been used as a sulfur source for the synthesis of metal sulfides, such as CoS, CdS, *etc.*[15] In addition, the amino acid L-asparagine has been used as an exfoliating agent for the delamination of CoAl LDHs.[16] Herein, we report an alkali-free hydrothermal synthetic protocol to prepare double metal hydroxides, also known as LDHs, and their delamination in a single step *via* the bottom-up approach using amino acids, such as arginine. In this method, the amino acid acts as both a precipitant and a stabilizer in the synthesis of two-dimensional LDH nanosheets. To the best of our knowledge, this is the first study to report the formation of double metal hydroxides or LDHs and their delamination in

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† Electronic supplementary information (ESI) available: LC-MS analysis of the supernatant solution at different temperatures, the mechanism of amino acid decomposition, and the electrocatalytic performance for CoAl-LDH and delaminated CoAl-LDH. See DOI: https://doi.org/10.1039/d5ma00035a

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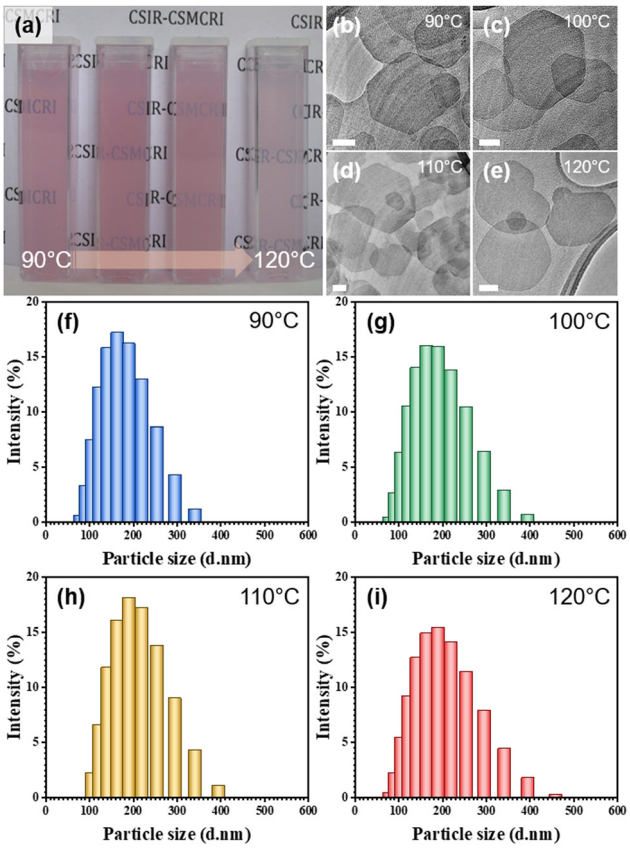

Fig. 1 (a) Digital photographs of delaminated LDH nanosheets in aqueous medium; (b)–(e) TEM images of delaminated LDH prepared at different temperatures (scale bar: 20 nm); (f)–(i) particle size distribution of delaminated LDH at the corresponding temperatures.

water without any treatment, using amino acids as hydrolyzing agents.

Delaminated LDH was synthesized using an amino acid-assisted hydrothermal method. Briefly, metal salts with a Co/Al atomic ratio of 3.0 (3 mmol Co^{2+} and 1 mmol Al^{3+} in 50 mL) were diluted in an appropriate amount of water, and L-arginine (9 mmol, sufficient for the complete hydroxylation of metals) was added. The mixture was hydrothermally treated at the desired temperature (90–120 °C) for 24 h. The final mixture was centrifuged at 7000 rpm to remove excess amino acids and the remaining metal solution. The precipitate settled during the first centrifugation step. Thus, the residue obtained was dispersed in decarbonized water to obtain a transparent colloidal dispersion of delaminated LDH, which did not settle even after centrifugation at 3000 rpm for 30 min, confirming the delamination of LDH (Fig. 1a).

The aqueous dispersion remained highly stable for more than three months. This enhanced stability can be attributed to the modification of LDH nanosheets by amino acids, as previously reported,[1b] possibly through electrostatic stabilization or coordination with metal hydroxide layers. Successful delamination of LDH was achieved within a temperature range of 90–120 °C using an amino acid-mediated hydrothermal synthesis method, as described in the ESI.† The degree of delamination

Table 1 Particle size and zeta potential of delaminated LDH[a]

Temp. (°C)	Zeta potential (mV)	Average particle size (nm)	Weight of LDH (g L^{-1})[b]
90	42.9 (51.5)	158 (205)	4.1 ± 0.5 (7.8 ± 0.3)
100	44.1 (52.5)	168 (200)	2.4 ± 0.2 (5.5 ± 0.5)
110	45.5 (56.1)	188 (221)	2.3 ± 0.4 (3.9 ± 0.2)
120	48.9 (59.4)	178 (233)	1.1 ± 0.2 (2.3 ± 0.4)

[a] Values in parentheses are derived from nitrate precursors, while others are from chloride precursors. [b] Calculated by drying the known volume of the sample at 80 °C.

decreased as the treatment temperature increased, as shown in Table 1. This can be attributed to the release of CO_2 at higher temperatures by the decomposition of amino acids (Scheme S1, ESI†) and is further supported by LC-MS analysis (Fig. S1, ESI†). A maximum delamination degree of 4.0 g L^{-1} was observed for a sample synthesized at 90 °C.

Particle size measurements showed that the average particle size increased with the temperature up to 110 °C. A further increase in temperature reduced the particle size. This can be attributed to the aggregation of LDH crystallites at higher temperatures, leading to particle sedimentation (Fig. 1f–i). This is reflected by the low degree of dispersion (g L^{-1}) of the sample, as indicated in Table 1. TEM images showed a thin, transparent plate-like structure of this colloidal sample, further confirming the delamination of LDH into nanosheets (Fig. 1b–e). Zeta potential measurements showed a positive surface charge ranging from 42–49 mV (Table 1), similar to previously reported delaminated LDH nanosheets.[10b,17]

Once the aqueous delaminated LDH suspension (obtained at 100 °C) contacted 0.1 M sodium carbonate solution, the nanosheets restacked as evidenced by the sedimentation caused by the intercalation of the carbonate anion, as confirmed by the powder X-ray diffraction (ICSD no. 056-0954) (Fig. 2), which showed strong basal reflections whose d_{003} value (7.48 Å) aligned with the reported values.[18] In contrast, when the same colloidal suspension was freeze dried, the PXRD of the obtained material showed an absence of basal plane reflections, suggesting a lack of stacking of nanosheets (thereby creating ordering along the '*c*' direction), corroborating the delamination into single sheets.

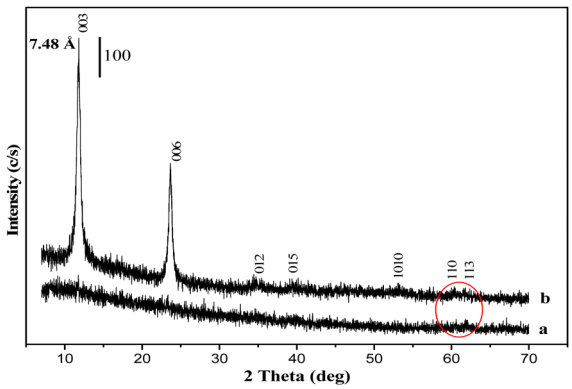

Fig. 2 PXRD of delaminated LDH synthesized at 100 °C: (a) freeze dried, and (b) after restacking with carbonate.

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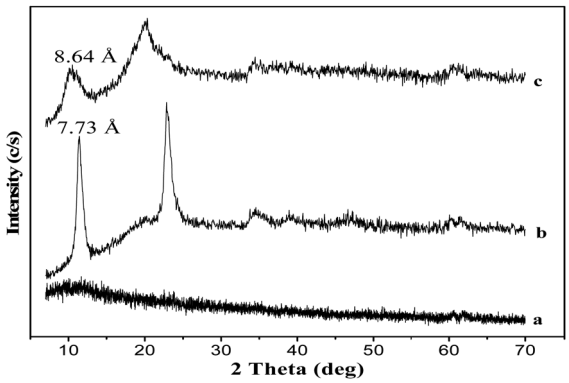
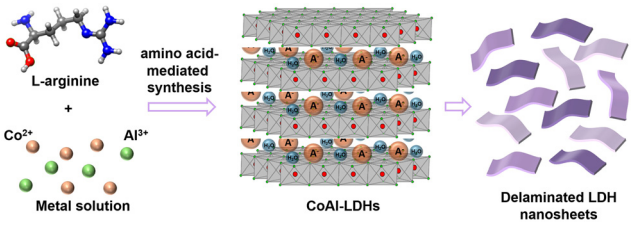


Fig. 3 PXRD of (a) the wet cake obtained using chloride precursor and the vacuum–dried wet cake obtained using (b) chloride and (c) nitrate metal precursor at 100 °C.

A weak reflection at $2\theta = 60.5^\circ$ corresponding to the (110) plane suggests the prevalence of ordering of nanosheets along the two-dimensional *ab* plane.

It has been reported that metal oxides or metal hydroxides are formed *via* the decomposition of water mediated by amino acids.[13a,14] The wet cake obtained after hydrothermal treatment at 100 °C showed poor crystalline broad reflection at lower angles, suggesting random and unordered stacking of nanosheets due to the functionalization with amino acid anions. The presence of amino acids in the LDH nanosheets was evidenced by Fourier transform infrared (FT-IR) spectroscopy (Fig. S2, ESI†). Interestingly, the wet cake dried under vacuum contained chloride or nitrate precursors in the interlayers when these corresponding metal precursors were used (Fig. 3). LC-MS analysis of the supernatant further suggested that LDH formation occurred *via* amino acid-assisted protonation and subsequent precipitation of metal hydroxides, as shown in Scheme 1. To further verify this phenomenon, metal salts alone were hydrothermally treated in the absence of amino acids, revealing the absence of metal hydroxides and suggesting the role of amino acids in assisting the hydrolytic decomposition.

To extend the applicability of the present synthetic protocol, other metal combinations, such as CoAl, MgAl, NiAl, ZnAl, ZnCr, and MgCr, were tested in duplicate. One set of samples was vacuum-dried, and the other set was subjected to delamination, as mentioned earlier. Here, metal nitrates served as the precursors and synthesis was conducted at 100 °C for 24 h. The vacuum-dried wet cake formed LDHs with nitrate as the interlayer anion (Fig. S3, ESI†). Delamination studies revealed that MgAl, NiAl, ZnAl, ZnCr, and CoAl LDHs underwent delamination to varying degrees, as demonstrated by photographs, dispersion levels, and zeta potential measurements (Fig. S4 and Table S1, ESI†). However, MgCr did not form LDHs under the experimental conditions (Fig. S3, ESI†). These findings present an alternative bottom-up, alkali-free, single-step synthesis approach for delaminated LDHs across a wide range of metal combinations.



Scheme 1 Amino acid-assisted precipitation and stabilization of LDH nanosheets through protonation-mediated metal hydroxide formation, with CoAl-LDH as an example.

As CoAl-LDH exhibits excellent electrolytic performance after delamination, its OER electrocatalytic activity was investigated in water electrolysis (Fig. S5, ESI†). The OER kinetic performance showed low overpotentials of 332 and 281 mV for the CoAl-LDH and delaminated CoAl-LDH, respectively. This clearly indicates that delaminated CoAl-LDH is more efficient and requires less potential to enhance OER activity. In addition, the smaller Tafel slope indicates rapid electron transfer and reaction kinetics of the delaminated CoAl-LDH catalyst. Stability studies of the delaminated CoAl-LDH catalyst revealed minimal potential loss and a stable current density, indicating robust conductivity, excellent mass activity, effective charge transport, and strong mechanical stability. Collectively, these findings demonstrate the superior electrocatalytic performance and long-term operational durability of the delaminated CoAl-LDH catalysts. Further details on the experimental setup, data analysis, and additional discussions are provided in the ESI.†

Conclusions

A series of delaminated LDHs with different metal combinations, such as CoAl, MgAl, NiAl, ZnAl, and ZnCr, were successfully prepared in a single step using an amino acid-assisted hydrothermal method *via* a bottom-up approach in an aqueous medium. Thus, the obtained delaminated LDHs were more stable than those prepared *via* conventional alkali-mediated synthesis, and the additional stability can be attributed to the functionalization of the LDH nanosheets with amino acid molecules. The approach presented here is promising for the synthesis of delaminated LDH and nitrate/chloride-containing LDH without requiring strict environmental restrictions. Additionally, it generates less waste than conventional alkali-mediated synthesis (requiring a large volume of water for washing to remove excess alkali); in our lab experiments, it was calculated that approximately 3 L of water is required for washing 10 g of LDH. The electrocatalytic performance showed that the delaminated CoAl-LDH catalyst had lower overpotential, Tafel slope and electrochemical impedance, and higher TOF and mass activity than CoAl-LDH. Electrocatalytic studies of delaminated CoAl-LDH catalysts offer potential for sustainable hydrogen generation.

Author contributions

Paulmanickam Koilraj: designed the research objectives and concept, conducted experiments, and provided ideas. Contributed significantly to the drafting of the manuscript. Rajathsing

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Kalusulingam: proposed experimental methods and designs and participated in conducting experiments. Contributed to the preparation of the manuscript draft. Kannan Srinivasan: analyzed data and reviewed and validated the research methodology. Conducted critical review and revision of the manuscript. Keiko Sasaki: led the review of the manuscript and managed the research project. Jun Ho Shim: handled manuscript writing, editing, submission, and overall project management.

Data availability

All data supporting this study are included in the article and its ESI.† Additional datasets are available from the corresponding author upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Ministry of Environment and Forests, New Delhi under the Environment Research Program (File No: 19/55/2005-RE) and the Council of Scientific and Industrial Research, New Delhi under Network Projects (CSC0114 and CSC0135) for financial assistance. P. K. thanks CSIR, New Delhi for the Senior Research Fellowship (31/28(134)/2011-EMR-1). J. H. Shim acknowledges support from the National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIT) (RS-2024-00339411).

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