Electronic Supporting Information

Alkali-free single-step synthesis of delaminated layered double hydroxide in water via amino acid-assisted hydrothermal method

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Synthesis of delaminated LDH by amino acid-mediated hydrothermal method

Delaminated LDH was synthesized using an amino acid–assisted hydrothermal method. Briefly, metal nitrate or chloride salts with Co/Al atomic ratio of 3.0 (3 mmol Co^{2+} and 1 mmol Al^{3+} in 50 mL) were dissolved in 50 mL water, and 1.6 g (9 mmol, stoichiometric amount required for the complete hydroxylation of metals) of L-arginine was added. The mixture was continuously stirred until the amino acids were completely solubilized. The mixture was transferred into a 70 mL Teflon-lined stainless-steel autoclave and treated hydrothermally at the desired temperature (90–120 °C) for 24 h. The autoclave was then cooled to room temperature. 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. The obtained residue was dispersed in decarbonized water, resulting in a transparent colloidal dispersion of delaminated LDH. The mixture was then centrifuged at 3000 rpm for 30 min. The supernatant containing the LDH was separated by decantation and designated as delaminated LDHs.

FT-IR analysis of amino acid anchoring on LDH nanosheets

FT-IR analysis of delaminated LDHs containing chloride and nitrate anions after freeze drying (Fig. S2) showed that the band at 3177 cm^{-1} corresponds to the –NH stretching vibration. The bands at 2928 and 2860 cm^{-1} correspond to –CH stretching vibrations.[1] The band centered at 1671 cm^{-1} is attributed to the –NH- stretching vibration of the ($CN_3H_5^+$) arginine side chain.[2] The –NH plane bending vibrations of the primary amine are observed at 1637 and 1023 cm^{-1}, while the –COO$^-$ asymmetric stretching vibration appears at 1573 cm^{-1}.[3] The symmetric and asymmetric stretching of C-C bonds appears at 1173 and 672 cm^{-1}. These results confirm that the amino acids were anchored onto the surface of the LDH nanosheets.

Electrochemical setup and methodology

The CoAl-LDH and delaminated CoAl-LDH catalysts were examined at ambient temperature using a P-45X/CHI 601E electrochemical workstation with a three-electrode setup in a 1.0 M KOH solution. Pt wire, Hg/HgO, and catalyst-coated nickel foam (detailed below) were used as the counter, reference, and working electrodes, respectively. Their electrocatalytic activities were assessed using linear sweep voltammetry (LSV), current versus time stability studies, and electrochemical impedance spectroscopy (EIS). To prepare the working electrode, drop-casting was employed. Briefly, upon dispersing the catalyst (8 mg) and activated carbon (2 mg) in ethanol (0.990 mL) and 5 wt% Nafion solution, the ink was ultrasonically dispersed for 15 min until it became uniform. The suspension (50 μL) was subsequently dropped onto the nickel foam electrode and dried. The mass loading of the catalysts on the Ni foam was 0.25 mg cm^{-2}. Prior to each experiment, the electrolyte was aerated with oxygen for 30 min. The CoAl-LDH and delaminated CoAl-LDH catalyst electrodes were tested in alkaline 1.0 M KOH electrolyte solutions. All the applied potentials were calibrated to the reversible hydrogen electrode (RHE) using the Nernst equation.

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0591 \times \mathrm{pH} + 0.098 \qquad (1)$$

The pH values of the three electrolytes were approximately 14. Linear sweep voltammetry (LSV) was recorded at a scanning rate 5 mV s^{-1} without iR drop corrections. The overall potential (η_{10}) for OER was determined by the calculation:

$$\eta\ (\mathrm{V}) = E_{\mathrm{RHE}} - 1.23 \qquad (2)$$

Electrochemical impedance spectroscopy (EIS) tests were conducted in 1.0 M KOH electrolyte from 0.1 Hz to 100 kHz at a potential of 500 mV. Chronoamperometry stability tests were conducted at a current density of 10 mA cm^{-2} for 12 h, as well as at multistep current densities of 10, 20, 50, and 100 mA cm^{-2} for 300 s (at each current density) in 1.0 M KOH electrolytes. The turnover frequency (TOF) was calculated under the assumption that every metal atom participated in catalysis, providing lower TOF limits.

$$\mathrm{TOF}_{\mathrm{OER}} = j \times S / 4 \times F \times m \qquad (3)$$

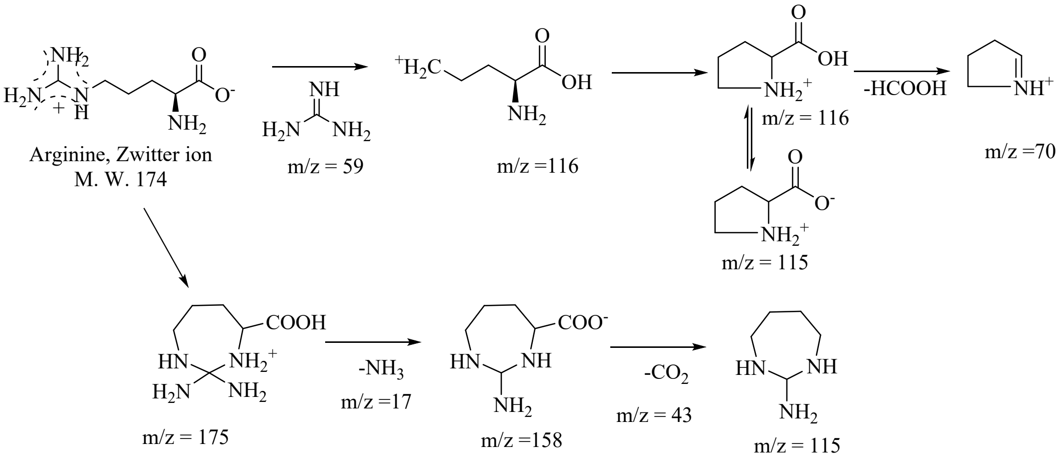
Mass activity was calculated as:

$$\text{Mass activity} = j\, m^{-1} \qquad (4)$$

where j (mA cm^{-2}) denotes the current density measured at $\eta_{\mathrm{OER}} = 1.60$ V, S denotes the surface area of the substrate, F is Faraday's constant (96485.30 C mol^{-1}), and m denotes the catalyst loading (mg cm^{-2}).

OER electrocatalytic activity and catalyst performance

For the electrocatalytic application of this work, we determined the OER electrocatalytic performance of the synthesized CoAl-LDH and delaminated CoAl-LDH catalysts using a three-electrode system in an alkaline 1.0 M KOH electrolyte solution. The polarization curves were recorded at a low scan rate of 5 mV s^{-1} without iR correction against Hg/HgO reference electrode and converted into reversible hydrogen electrode (RHE) scale. As shown in Fig. S5a, the polarization curves show the overpotential required for delaminated CoAl-LDH to reach the lowest overpotential of 281 mV at a current density of 10 mA cm^{-2} compared to CoAl-LDH (332 mV), indicating that delaminated CoAl-LDH is more efficient due to its lower potential requirement for promoting OER activity. The Tafel slopes appeared to be smaller for delaminated CoAl-LDH (85 mV dec^{-1}) than for CoAl-LDH (96 mV dec^{-1}). This represented the rapid reaction kinetics of delaminated CoAl-LDH (Fig. S5b). It involved a rapid oxidation mechanism consisting of the following steps: $M + OH^- \rightarrow M\text{-}OH + e^-$; $M\text{-}OH + OH^- \rightarrow M\text{-}O + H_2O + e^-$; $M\text{-}O + OH^- \rightarrow M\text{-}OOH + e^-$; $M\text{-}OOH + OH^- \rightarrow M\text{-}OO^- + H_2O + e^-$; $M\text{-}OO \rightarrow M + O_2$).[4] As shown in Fig. S5c, the mass activity and TOF were enhanced by delaminated CoAl-LDH. For instance, The TOF value increased from 2.17 to 10.69 s^{-1} owing to the delamination. Electrochemical impedance spectroscopy (EIS) was performed to gain insight into boosted activity. The smaller semicircle in the Nyquist plot (Fig. S5d) indicates that the delaminated CoAl-LDH has lower charge-transfer resistance than CoAl-LDH. The efficacy of the catalyst was evaluated using overpotential, Tafel slope, mass activity and turnover frequency (TOF). Multistep electrolysis of catalysts was evaluated via chronoamperometry at current densities 10, 20, 50, 90, and 100 mA cm^{-2} for 300 s at each current density (Fig. S5e). Additionally, the stability of the delaminated CoAl-LDH catalyst was evaluated using constant-current electrolysis as shown in Fig. S5f. The potential of the delaminated CoAl-LDH catalyst increased slightly over 12 h at current densities 10 mA cm^{-2}, which revealed potential retention of its initial activity and demonstrated the high level of mass transport of OH$^-$ and O_2 in the OER electrocatalytic process.[5, 6]



Scheme S1. Mechanism of thermal decomposition of amino acids during hydrothermal synthesis.

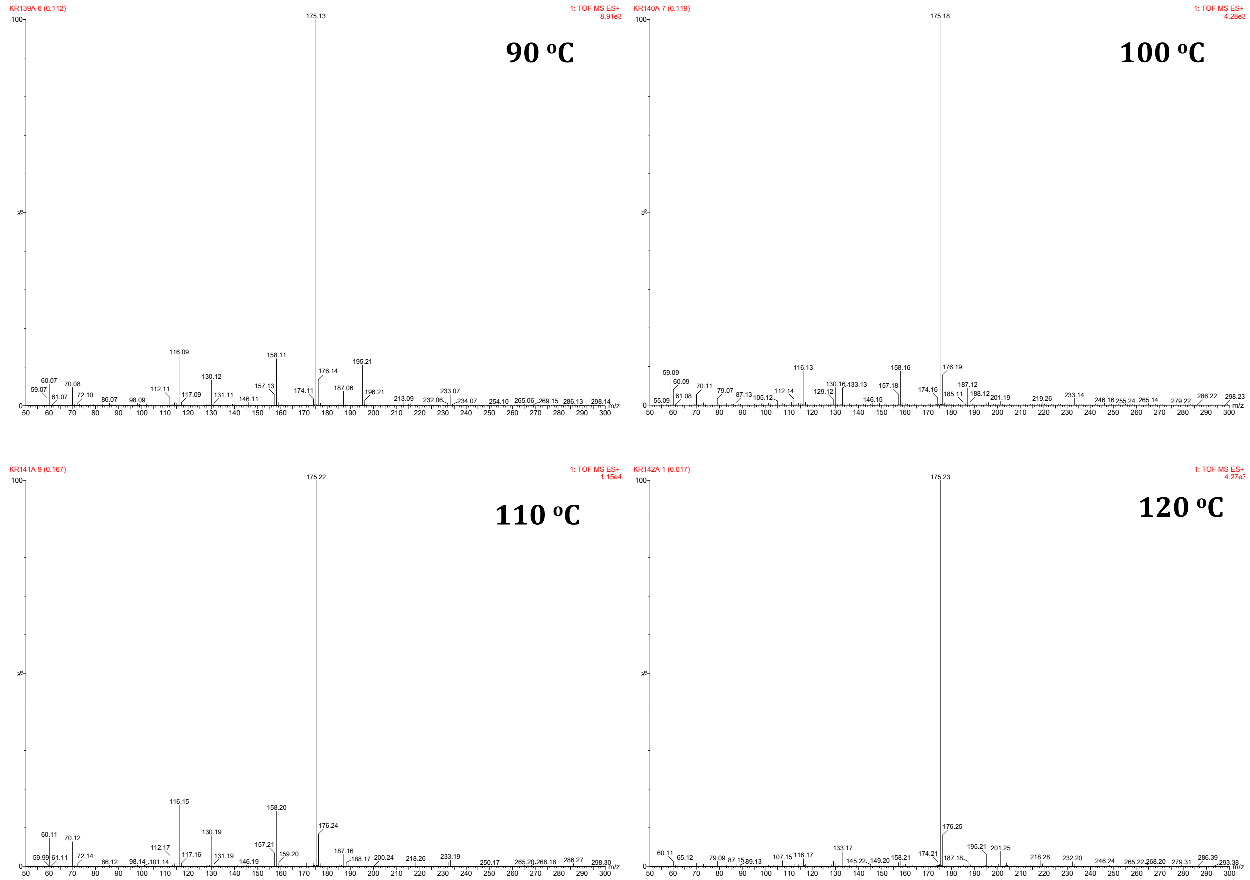


Fig. S1. LC-MS Spectra of supernatant obtained in hydrothermally treated L-arginine during LDH synthesis at different temperatures.

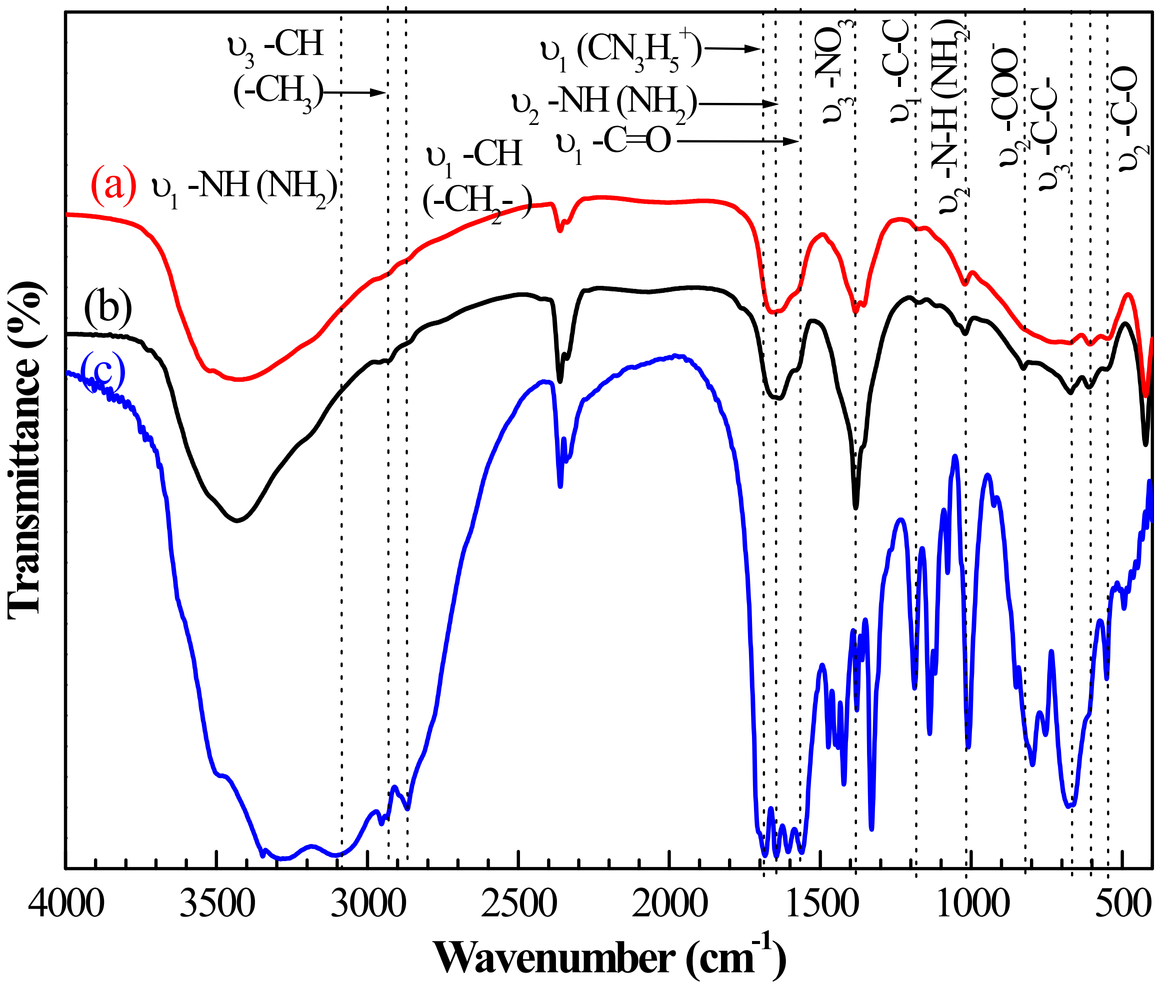


Fig S2. FT-IR Spectra of delaminated LDH synthesized at 100 °C after freeze drying (a) chloride precursor, (b) nitrate precursor, and (c) powdered L-arginine.

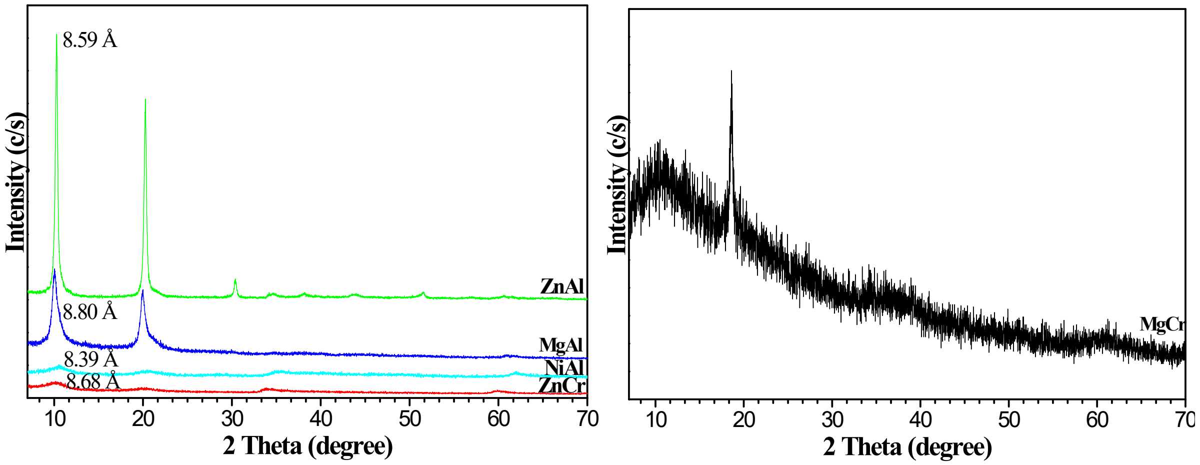


Fig. S3. PXRD patterns of vacuum-dried wet cakes synthesized using different combinations of nitrate precursors via arginine-mediated hydrothermal synthesis at 100 °C. Synthesis conditions: M(II)/M(III) atomic ratio of 3.0 (3 mmol M^{2+} and 1 mmol M^{3+} in 50 mL), arginine (1.6 g, 9 mmol), and reaction time of 24 h.

Fig. S4. Photographs of delaminated LDHs synthesized using different combinations of nitrate precursors via arginine-mediated hydrothermal synthesis at 100 °C. Synthesis conditions are the same as in **Fig. S3**, with the wet cakes delaminated.

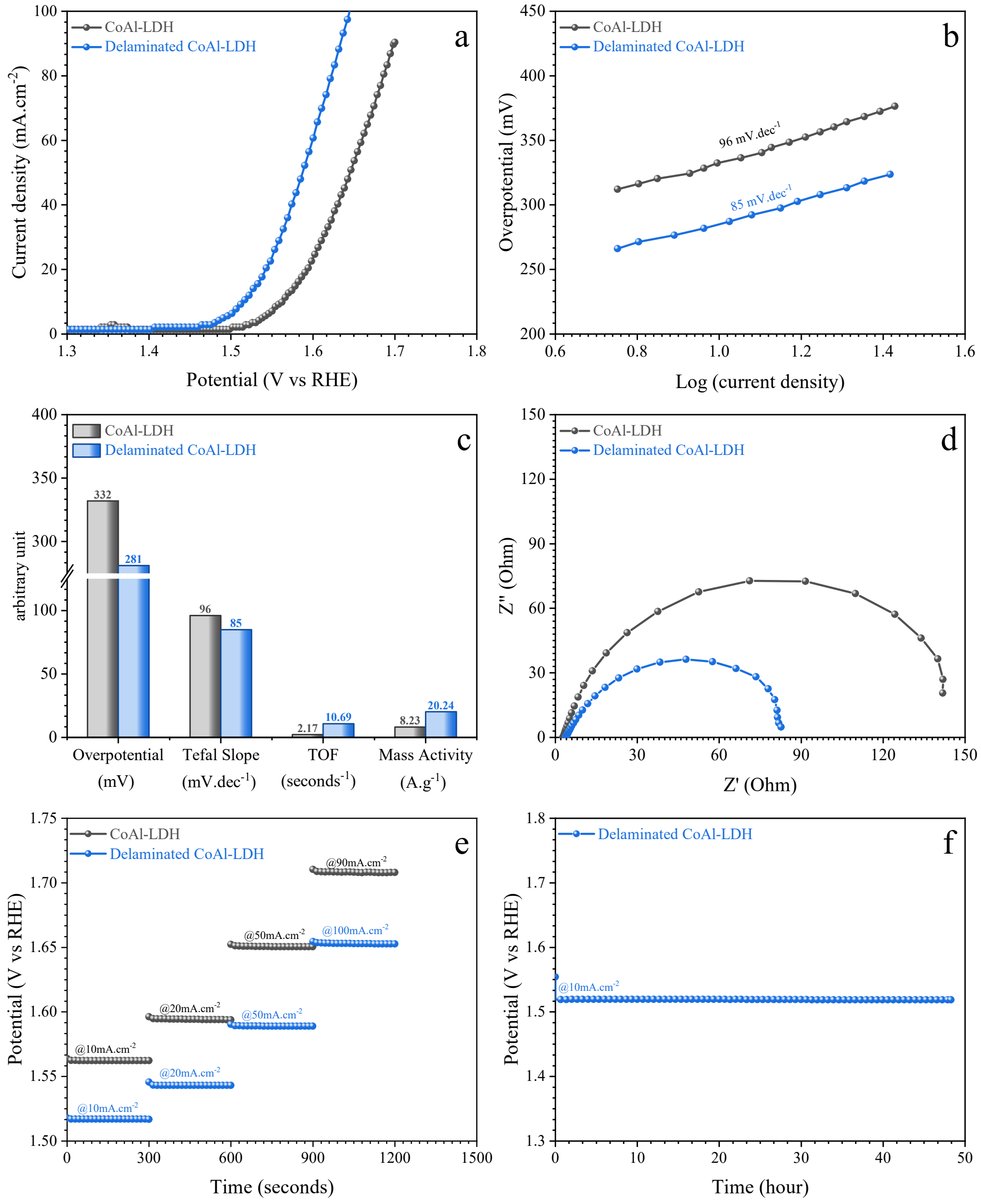


Fig. S5. OER electrocatalytic performance comparison of CoAl-LDH and delaminated CoAl-LDH: (a) polarization curves, (b) Tafel slopes, (c) comparison of overpotential, Tafel slope, TOF, and mass activity, (d) Nyquist plots, (e) multistep chronoamperometry studies at varying current densities (10, 20, 50, 90, 100 mA cm^{-2} for 300 s each), and of CoAl-LDH and delaminated CoAl-LDH, and (f) chronopotentiometry stability of delaminated CoAl-LDH at 10 mA cm^{-2} over 12 h.

Table S1. Particle size and zeta potential of delaminated LDH synthesized at 100 °C

delaminated LDH	**zeta potential (mV)**	**average particle size (nm)**	**weight of LDH (g L^{-1})[a]**
CoAl-Cl	44.1 (52.5)	168 (200)	2.4 ± 0.2 (5.5 ± 0.5)
CoAl-NO_3	41.7	322.1	3.4 ± 0.3
MgAl-NO_3	41.7	201.5	3.5 ± 0.2
NiAl-NO_3	34.1	467.2	3.2 ± 0.4
ZnAl-NO_3	53.8	350.3	1.2 ± 0.4
ZnCr-NO_3	38.8	466.5	4.0 ± 0.6

[a] Calculated by drying known volume of the sample at 80 °C.

References

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