

Oriented printable layered double hydroxide thin films via facile filtration

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Electronic Supplementary Information

Figure S1. FTIR spectra of carbonated CoAl and NiAl-LDH and their anion exchange samples: CoAl-CO₃-LDH (a₁), CoAl-Cl-LDH (a₂), CoAl-NO₃-LDH (a₃), NiAl-CO₃-LDH (b₁), NiAl-Cl-LDH (b₂), and NiAl-NO₃-LDH (b₃).

Figure S2. SEM images of CoAl-Cl-LDH (a) and CoAl-NO₃-LDH (b).

Figure S3. SEM images of NiAl-Cl-LDH (a) and NiAl-NO₃-LDH (b).

Figure S4. XRD patterns of freshly prepared CoAl-LDH wet film and subsequently dried film. Insert is the proposed mode of arrangement of CoAl-LDH nanosheets.

Figure S5. Photos of LDH colloids mixed with various anions. The pink serial is of CoAl-LDH colloids, while the green one is of NiAl-LDH colloids.

Figure S6. TGA curves of (a) PEO, restored NiAl-LDH and NiAl-PEO-LDH samples, (b) APAM, restored NiAl-LDH and NiAl-APAM samples.

Figure S7. SEM images of CoAl-PEO (a, b) and NiAl-PEO (c, d) hybrid films at low (a, c) and high (b, d) magnifications.

Figure S8. Chemical structure of sulforhodamine 101 (a) and photographs of sulforhodamine 101-incorporated CoAl-LDH thin films under 365 nm UV irradiation (b, c).

Figure S9. SEM images of NiAl-LDH coated Al sheet before and after immersion in 3.5% aqueous NaCl solution for 6 days at room temperature.

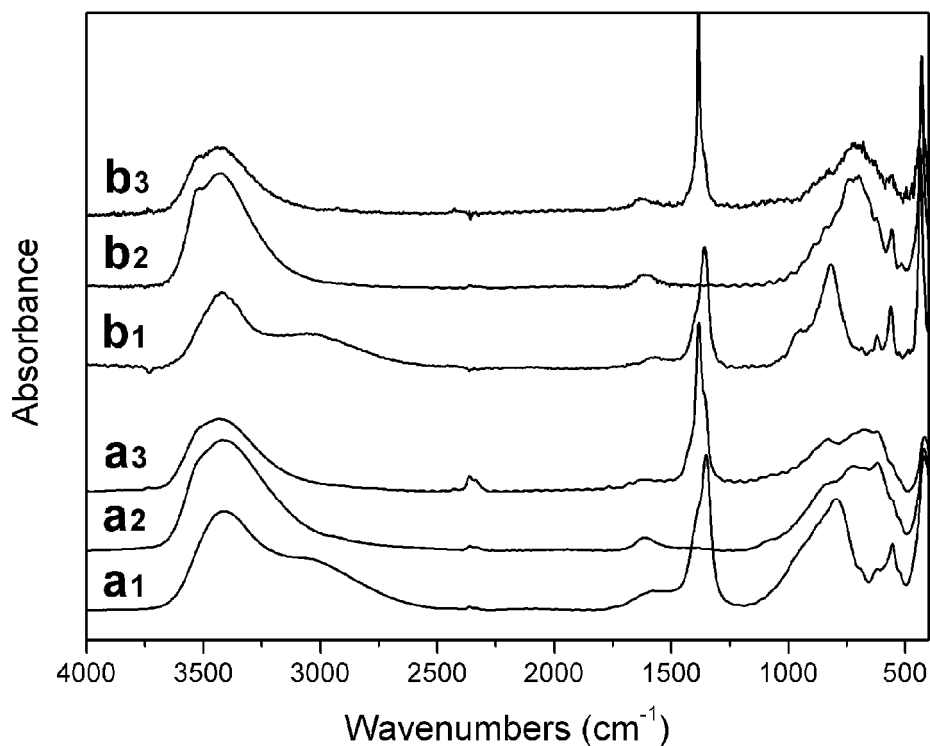


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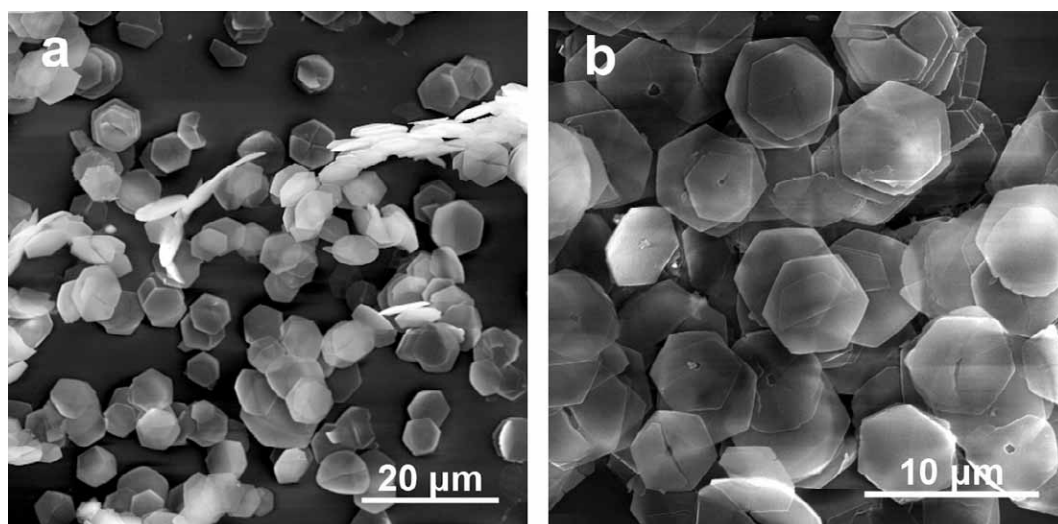


Figure S2. SEM images of CoAl-Cl-LDH (a) and CoAl-NO₃-LDH (b).

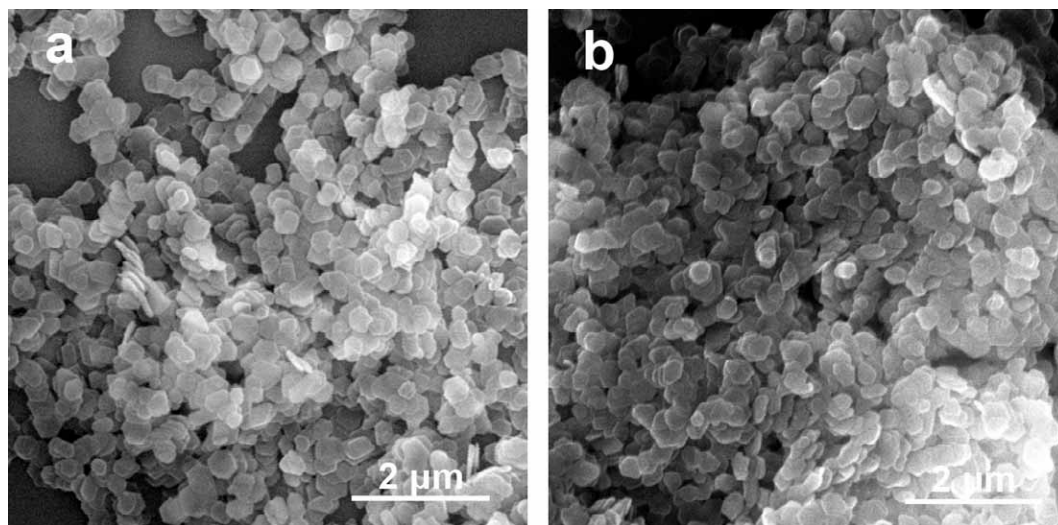


Figure S3. SEM images of NiAl-Cl-LDH (a) and NiAl-NO₃-LDH (b).

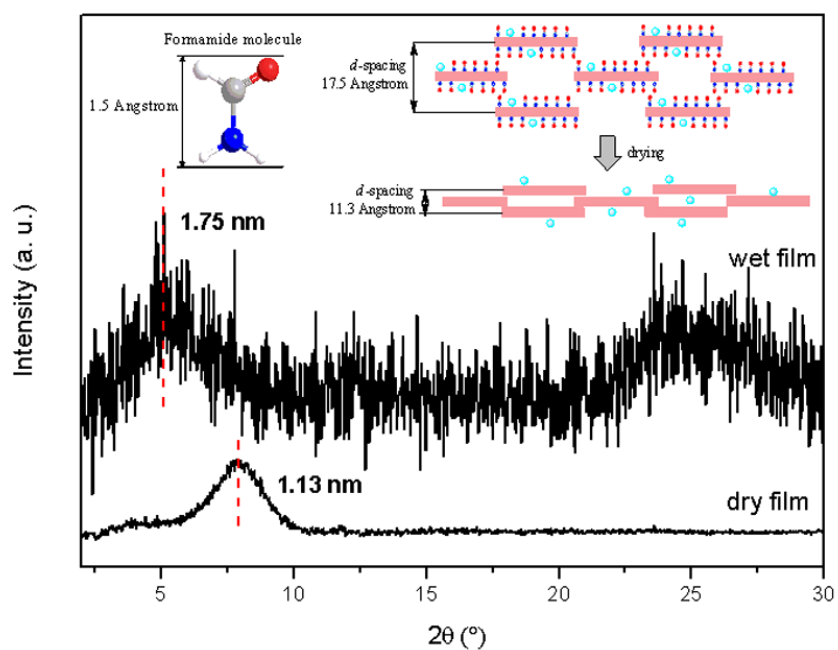


Figure S4. XRD patterns of freshly prepared CoAl-LDH wet film and subsequently dried film. Insert is the proposed mode of arrangement of CoAl-LDH nanosheets.

Notes: Formamide, CH_3NO , which is the simplest amide, is thought to be a mixture of the origin form (I) and the dipolar form (II).¹⁻⁴ As a result of strong resonance interaction of the p-type N lone pair with the carbonyl π system, negative charge is generated at the site of carbonyl oxygen atom. When positively charged LDHs were delaminated in formamide, formamide molecules would be adsorbed on the surface of LDHs in the form of oxygen atoms facing to LDHs. It is estimated that the height of formamide molecule in that orientation is about 1.5 angstrom. Fig. S4 shows the XRD patterns of freshly prepared CoAl-LDH wet film and subsequently dried sample. After drying, the d -spacing of CoAl-LDH film was decreased by 6.2 angstrom (from 1.75 nm to 1.13 nm), which is approximately the height of 4 layers of adsorbed formamide molecules. Therefore, it also indicates that CoAl-LDHs are packed in staggered arrangement.

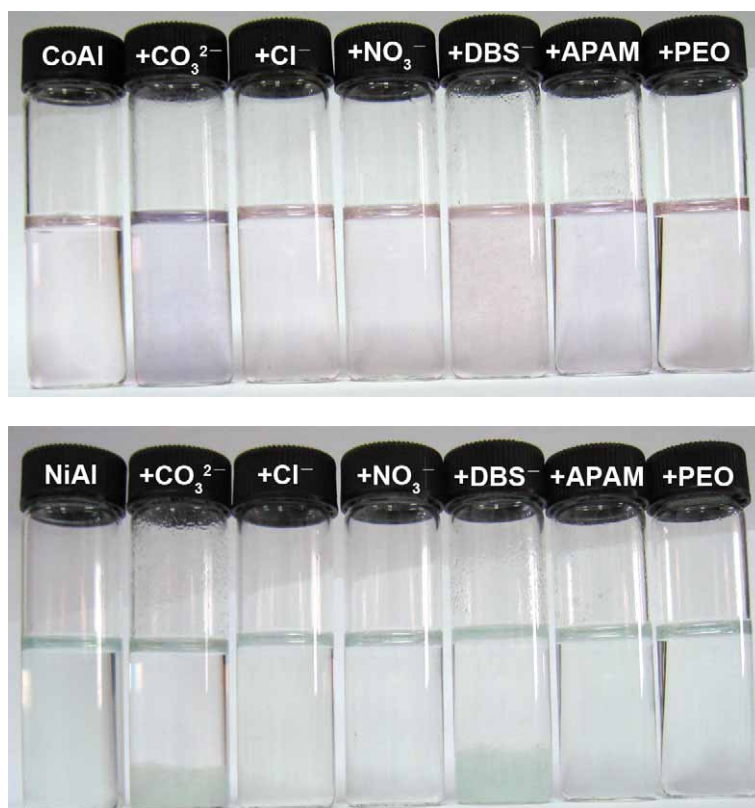
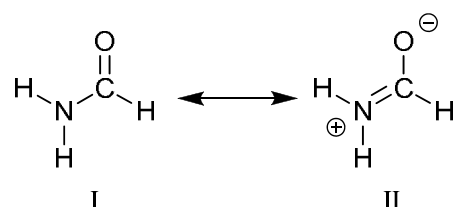


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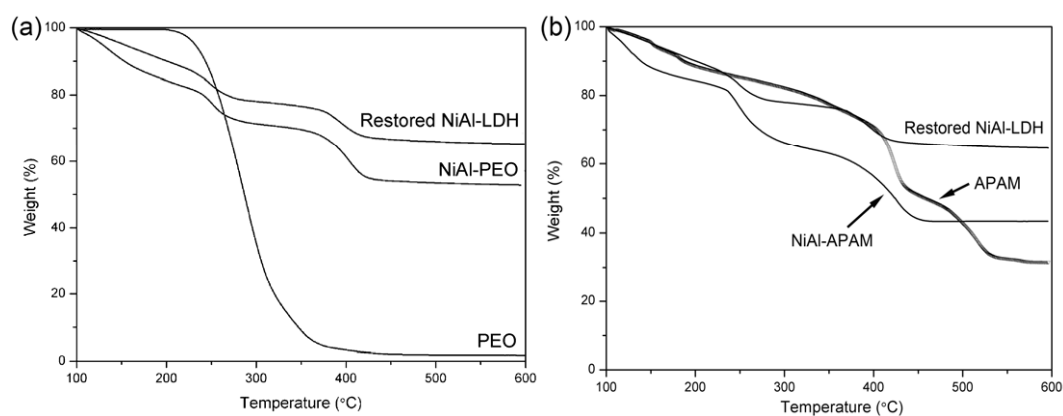


Figure S6. TGA curves of (a) PEO, restored NiAl-LDH and NiAl-PEO-LDH samples, (b) APAM, restored NiAl-LDH and NiAl-APAM samples.

Characterization methods: Thermogravimetric analysis (TGA) was performed from 100 to 600 °C at a heating rate of 20 °C/min using a Perkin Elmer Pyris-1 TGA under air atmosphere. The air flow was set at 20 mL/min. Restored NiAl-LDH, NiAl-PEO-LDH and NiAl-APAM-LDH samples were generated from centrifugation of colloidal dispersion of LDHs in formamide at 14000 rpm for 15 min. After centrifugation, the samples were washed by ethanol for several times and dried under vacuum at 80 °C.

Discussion: In air, polyethylene oxide (PEO) reaches the largest decomposition at about 285°C and degrades completely at 600°C (content of residue is 1.5%, which may be the content of undegraded impurities). The decomposition of restored NiAl-LDH undergoes two processes: decomposition of absorbed molecules and subsequent phase transition. The residue contents of restored NiAl-LDH and NiAl-PEO-LDH are 65% and 55%, respectively. Therefore, the content of PEO included in NiAl-PEO-LDH is about 10%. The calculated content of APAM in NiAl-APAM-LDH is more complex. The residual contents of APAM and NiAl-APAM at 600°C in air are 32% and 44%, respectively. The weight fraction of NiAl-LDH in NiAl-APAM multiplying 65% plus the weight fraction of APAM in NiAl-APAM multiplying 32% equals to 44%. Therefore, the weight fraction of APAM is calculated to be about 64%.

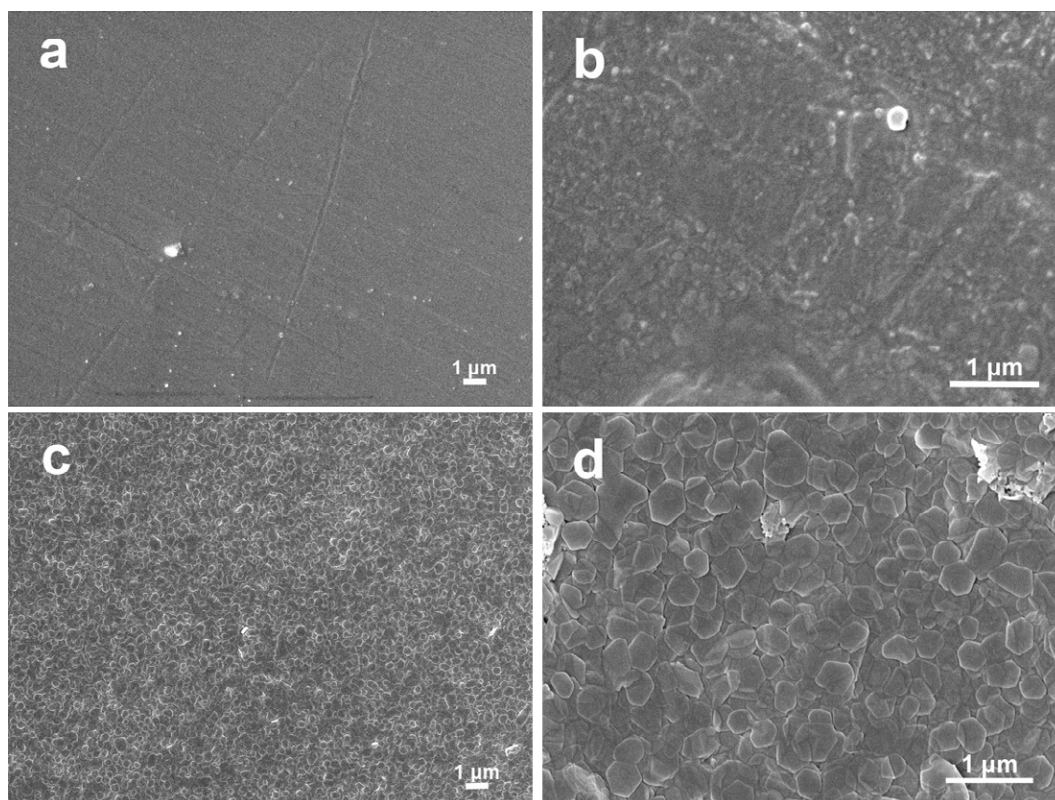


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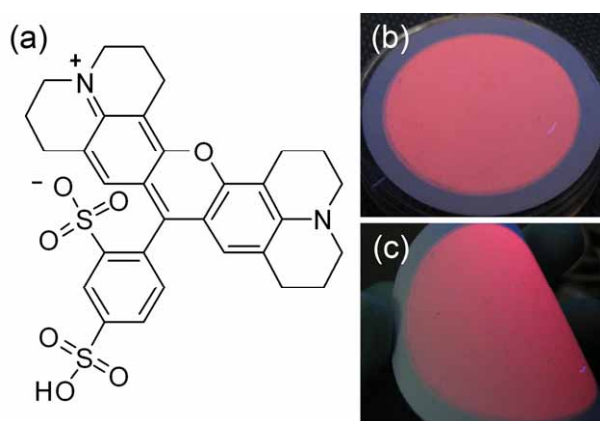


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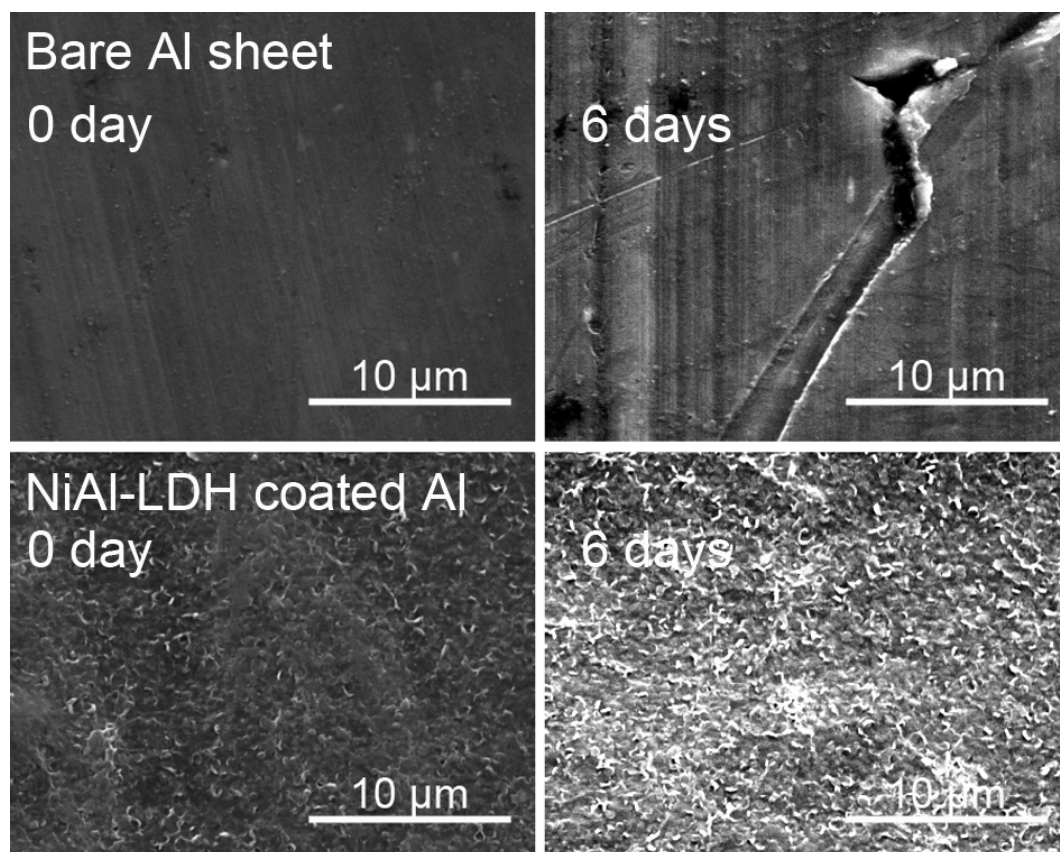


Figure S9. SEM images of NiAl-LDH coated Al sheet before and after immersion in 3.5% aqueous NaCl solution for 6 days at room temperature.

References

1. K. B. Wiberg and P. R. Rablen, *J. Am. Chem. Soc.*, 1993, **115**, 9234-9242.
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