

Large Continuous, Transparent and Oriented Self-supporting Films of Layered Double Hydroxides with Tunable Chemical Composition

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Supplementary Information

Materials: Tb_4O_7 was from Beijing Founder Dongan Rare Earths New Materials Co. Ltd. All other reagents were of AR grade and obtained from Beijing Yili Fine Chemical Reagent Co. and used without further purification. Deionized water with a conductance below 10^{-6} S cm^{-1} was decarbonated by boiling and bubbling N_2 before use in any synthesis or purification steps.

Synthesis of colloidal [MAl-NO₃] LDHs (M = Zn, Ni) by the SNAS method¹⁴: An aqueous solution of $M(NO_3)_2 \cdot 6H_2O$ (1.2 M) + $Al(NO_3)_3 \cdot 9H_2O$ (0.6 M) and an aqueous solution of NaOH (3.42 M) were simultaneously added to a colloid mill with rotor speed of 3000 rpm and mixed for 1 min. The resulting suspension was removed from the colloid mill, aged at 100 °C for 8 h. The final suspension was washed several times with water by centrifugation, and then stored as a slurry under nitrogen for later use.

Synthesis of colloidal [ZnAl-Tb(EDTA)] LDH by an ion-exchange method¹⁵: A mixture of Tb_4O_7 (15 mmol) and H_4EDTA (60 mmol) was refluxed in water (100 ml) until the solid had completely dissolved. Aqueous NaOH solution (0.5 M) was added until the pH reached 6. After slow evaporation of the solution, a white powder was obtained which was washed with cold water to afford $Na[Tb(EDTA)] \cdot 3H_2O$. A portion of the ZnAl-NO₃ LDH slurry (ca. 2 mmol of NO₃⁻) was added to 50 ml water and stirred for several minutes. The resulting suspension was added dropwise to a solution of $Na[Tb(EDTA)] \cdot 3H_2O$ (6 mmol) in 50 ml water. After adjusting the pH to 6, the resulting heavy gel was aged under an N_2 atmosphere at 65 °C for 8 h.

Measurements: Powder XRD patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu K α radiation. Elemental analysis of the metal content was performed with an ICPS-7500 inductively coupled plasma optical-emission spectrometer. C, H, and N elemental analysis was carried out with an Elementar Vario elemental analyzer. The SEM images were obtained on a Hitachi S-4700 field emission scanning electron microscope at 20 kV, with the surface of the samples coated with a thin gold layer to avoid a charging effect. Samples were either self-supporting films prepared by evaporation of a dilute aqueous suspension of the LDH nanoparticles or powders ground after drying at 60 °C.

Fig. S1 Transmittance of a transparent self-supporting [ZnAl-NO₃] LDH film with 24 μm thickness.

