Oriented films of layered rare earth hydroxide crystallites self-assembled at the hexane/water interface

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Electronic Supplementary Information

Experimental details

In a typical experiment, 20 mg of rare earth hydroxide crystallites of $Eu(OH)_{2.5}Cl_{0.5}\cdot 0.9H_2O$ were dispersed in 40 mL of Milli-Q water in a 5-cm-diameter glass beaker with ultrasonic treatment for 1-2 min. Hexane (10 mL) was added to the beaker to produce a hexane (top)/ water (bottom) interface with an area close to 10 cm^2. Ethanol (1.5 mL) was added to the interface at a low rate of 0.6 mL min^{-1}. Upon the addition of ethanol, the rare earth hydroxide crystallites became trapped at the interface. Then most of the hexane at the top of the beaker was carefully removed by syringe, and the densely packed film was transferred to quartz glass or silicon substrate by pulling the substrate out of the liquid phase. Prior to the transfer procedure, the substrates (silicon wafer or quartz) were cleaned by a standard procedure involving immersion in a 1/1 HCl/CH_3OH solution and then in concentrated H_2SO_4 for 30 min each. The clean substrates were treated with a polyethylenimine (PEI, 2.5 g dm^{-3}) and poly(sodium styrene 4-sulfonate) (PSS, 1.5 g dm^{-3}) aqueous for 20 min each and rinsed with water, respectively. After deposition, the monolayer film was immersed in ethanol with moderate ultrasonic treatment (42 kHz, 90W) for a few seconds, and then dried in air at a controlled humidity of 70% at room temperature for 3-5 h. The multilayer film was fabricated in a layer-by-layer fashion. Firstly, a monolayer film was fabricated at the hexane/water interface, and then transferred onto a substrate. Secondly, a monolayer film was fabricated at the hexane/water interface in another vessel, and then was transferred onto the substrate covered with the first layer. This procedure was repeated several times to prepare multilayer films.

The anion-exchange experiments were carried out by immersing a monolayer film into an aqueous solution of 1M $NaNO_3$ and 0.5M sodium dodecylsulfate (SDS, $C_{12}H_{25}OSO_3Na$) for 72 h at room temperature, respectively. Subsequently the film was washed in a copious amount of Milli-Q water and then in ethanol, and dried in air at a controlled humidity of 70% at room temperature for 3-5 h.

XRD patterns of the monolayer film were obtained by a Rigaku Rint-2000 diffractometer (Cu Kα, λ=1.5405Å). The films were examined using a Keyence VE8800 scanning electron microscope at an accelerating voltage of 10 kV. The photoluminescence excitation and emission spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. Tapping-mode AFM images were obtained using a Seiko Instruments SPA-400 AFM system with a Si-tip cantilever (20 N m^{-1}) in DFM mode.

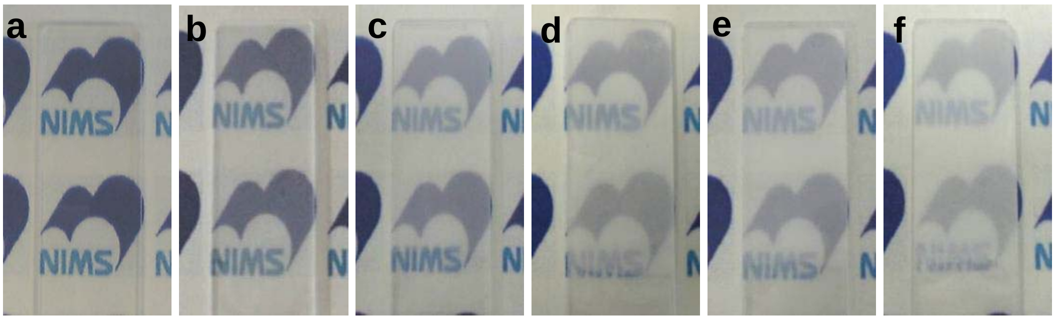

Figure S1. Photograph of multilayer films of $Eu(OH)_{2.5}Cl_{0.5}\cdot 0.9H_2O$ crystallites deposited on the quartz glass substrate: (a) quartz glass substrate (0 layer); (b) 1 layer; (c) 2 layers; (d) 3 layers; (e) 4 layers; (f) 5 layers.

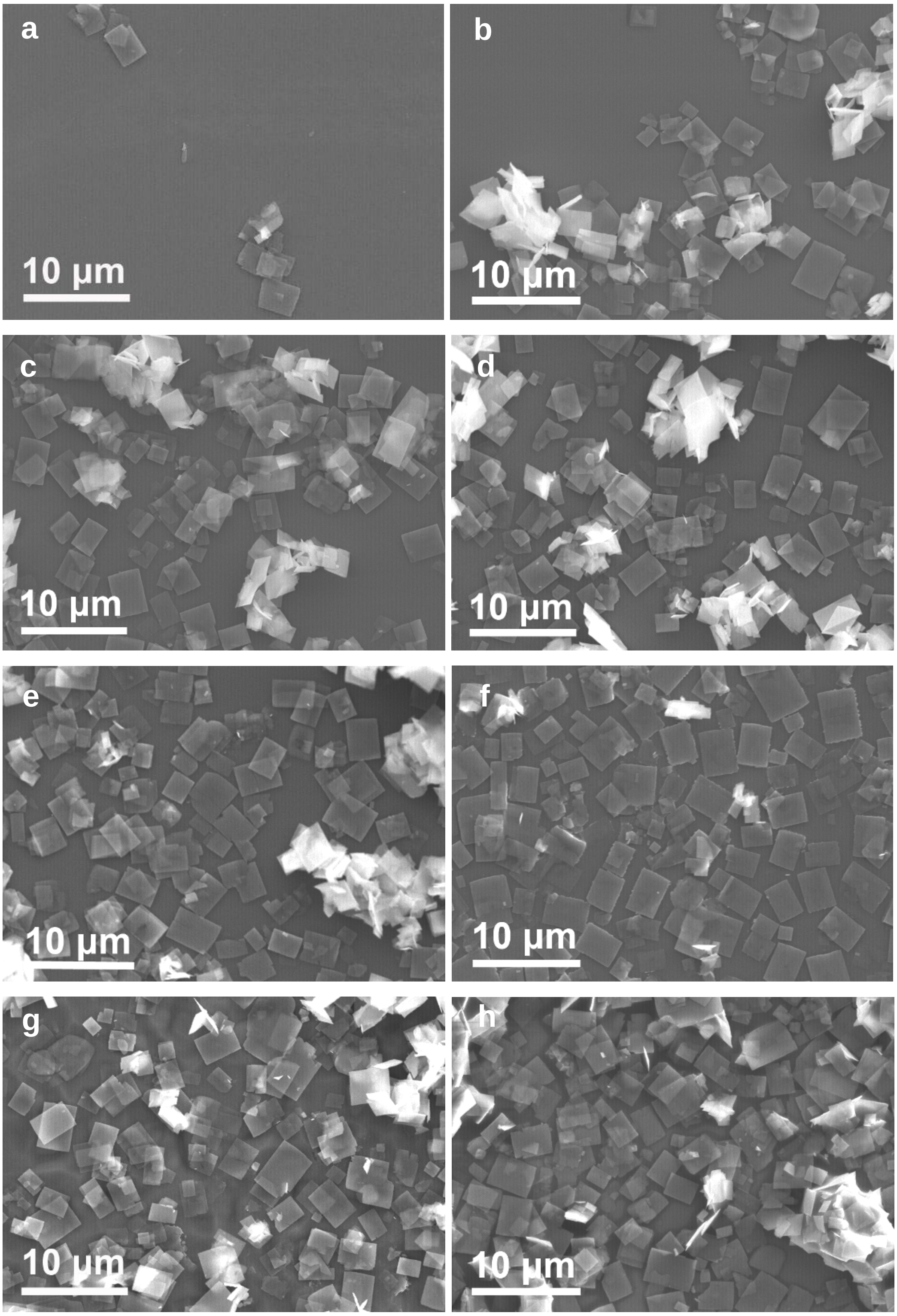

Figure S2. The SEM images of the film (before ultrasonic treatment) obtained using different amounts of ethanol: (a) 0 mL; (b) 0.1 mL; (c) 0.3 mL; (d) 0.5 mL; (e) 1.0 mL; (f) 1.5 mL; (g) 3.0 mL; (h) 5.0 mL.

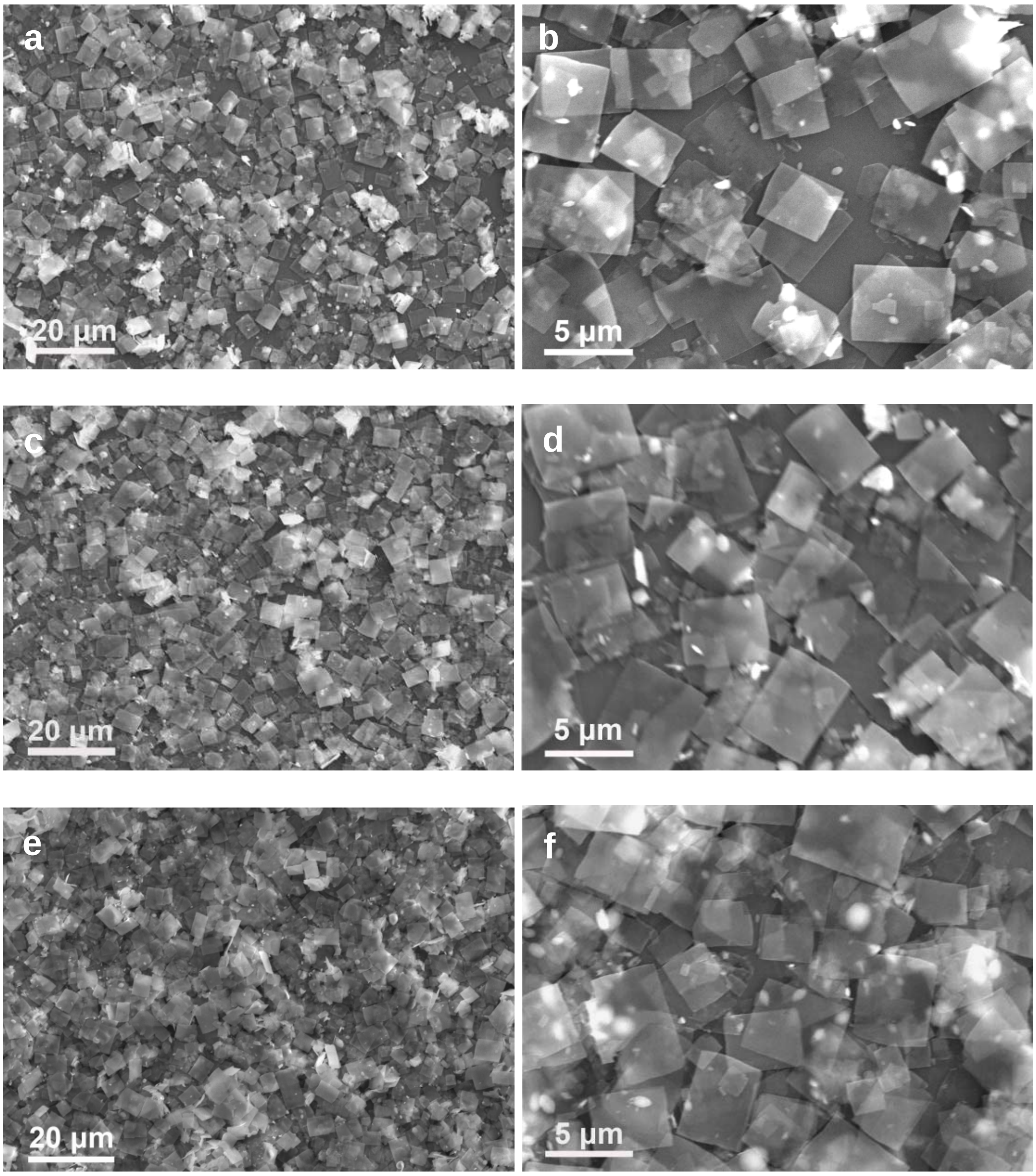

Figure S3. SEM images of the multilayer films on silicon substrate: (a, b) 2 layers; (c, d) 3 layers; (e, f) 4 layers.

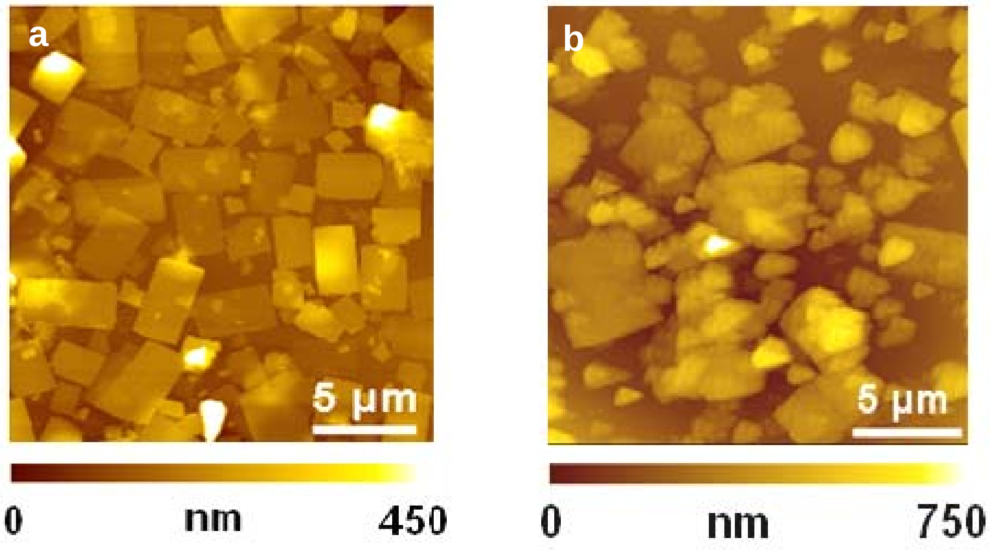

Figure S4. Typical AFM images of the monolayer film: (a) Cl^- form before ion-exchange reaction; (b) $C_{12}H_{25}OSO_3^-$ form after ion-exchange reaction.