Supplementary Material (ESI) for Chemical Communications

Hierarchical Films of Layered Double Hydroxides by Using a Sol-Gel Process and their Maneuverable Application in Water Treatment

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1. Preparation of AlOOH primer sol

$Al(OPr)_3$ (11.3 g) was dissolved in 100 ml of deionized water by stirring at 85 °C for 20 min. HNO_3 (1 M) was then slowly added dropwise to the solution for the hydrolysis of $Al(OPr)_3$, and the solution pH was held in the range 3~4. The solution was stirred at 85 °C for 2 h and then slowly cooled to room temperature. The boehmite (AlOOH) solid was obtained after evaporation of water. Through milling, the boehmite (5.8 g) were added in 107 ml of deionized water by stirring at 84 °C for 1 h. Then HNO_3 (9.5 ml, 1M) was slowly added dropwise to the solution and refluxed gently with stirring for 6 h. The boehmite (Al(OOH)) primer sol was obtained after slow cooling to room temperature.

2. Preparation of AlOOH/substrate film

Paper, cloth and sponge were employed as the man-made templates for fabricating the LDH films. The substrates of Paper (Hangzhou Te Zhong Paper Co., Ltd., Φ 9cm, medium speed), cloth (cotton) and sponge (Polyurethane) were cleaned with DI water several times to eliminate any contaminations. The substrates were immersed into the boehmite (AlOOH) primer sol by the use of the Layer-by-Layer Deposition Robots (Riegler & Kirstein GmbH). The substrates were placed vertically in the boehmite

sol for 5 min, followed by withdrawing the substrate out of the sol with a ascent velocity of 0.05 cm/min. The resulting films were dried in air for 15 min. The whole process (immersion, withdrawing, drying) was repeated 40 times.

3. Preparation of M( )Al-LDH (M= Zn, Ni, Mg)/substrate films

Preparation of ZnAl-LDH/substrate film: The ZnAl-NO_3 LDH film was prepared by an *in situ* growth technique, according to our previous report.[1] $Zn(NO_3)_2 \cdot 6H_2O$ (0.01 mol) and NH_4NO_3 (0.06 mol) were dissolved in deionized water (100 mL), and the 1% ammoniaol solution was then slowly added until the pH reached 6.5. The AlOOH/substrate was immersed into the above solution in a glass vessel at 75 °C for 36 h. Finally, the substrate was removed, rinsed with ethanol, and dried at 70 °C for 12 h.

Preparation of NiAl-LDH/substrate film: the NiAl-NO_3 LDH film was prepared by *in situ* crystallization on AlOOH/substrate. In a typical procedure, 0.1 mol of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.6 mol of NH_4NO_3 were dissolved in deionized water to form a clear solution with a total volume of 300 ml, and the pH was adjusted to 5.9 by adding diluted ammonia (1% NH_4OH). The AlOOH/substrate was placed vertically in a glass vessel at 75 °C for 18 h. Finally, the substrate was removed, rinsed with ethanol, and dried at 70 °C for 12 h.

Preparation of MgAl-LDH/substrate film: The MgAl-CO_3 LDH film was fabricated by *in situ* growth on AlOOH/substrate by means of urea hydrolysis similar to previous report by our group.[2] A solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.016 mol) and urea (0.097 mol) dissolved in 300 ml deionized water was placed in a 600 mL glass vessel. The as-prepared AlOOH/substrate was immersed into the solution. The glass vessel was sealed and maintained at 80 °C for 1 day. After cooling, the substrate was washed with ethanol, and dried at 70 °C for 12 h.

4. Preparation of the ZnAl-LDH powder sample:

The ZnAl-LDH powder sample (Zn/Al=2.0) was synthesized by the hydrothermal method reported previously.[3] A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.2×10^{-1} M) and $Al(NO_3)_3 \cdot 9H_2O$ (6.0×10^{-2} M) in deionized water (2.0×10^{-4} m^3) was added dropwise over 2 h to a solution of NaOH (3.1×10^{-1} M) and $NaNO_3$ (2.1×10^{-1} M) in water (1.0×10^{-4} m^3). The mixture was held at 70 °C for 24 h. The precipitate was separated by centrifugation, washed thoroughly with water, and dried at 70 °C for 20 h.

5. Sample Characterization

The powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.15418 nm) at 40 kV, 30 mA, with a scan step of 0.02° and a 2θ angle ranging from 8° to 70°. The morphology of the film samples was investigated using a Hitachi S-3500N scanning electron microscope (SEM) with an accelerating voltage of 20 kV.

6. Water Treatment Experiment

The water treatment activities of the ZnAl-LDH/paper film was evaluated by the adsorption of two dyes (sulforhodamine B, Congo red) and $K_2Cr_2O_7$. Firstly, 4 ml of sulforhodamine B (10 ppm), Congo Red (100 ppm) or $K_2Cr_2O_7$ (10 ppm) solution was added respectively to a typical quartz cell, and then 8 cm^2 of ZnAl-LDH/paper film sample was immersed into the solution. The UV-vis absorption spectra of the solution as a function of adsorption time were recorded with a spectrophotometer (Beijing PGENERAL TU-1901). The inductively coupled plasma emission spectrometer (ICP-ES) (Shimadzu ICPS-7500) was used to measure the chromium concentration in solution. The blank adsorption was carried out following the same procedure by using the pristine filter paper without any treatment. The powder sample of ZnAl-LDH with the same mass to the film was also evaluated as a comparison adsorbent.

7. Characterization and Results

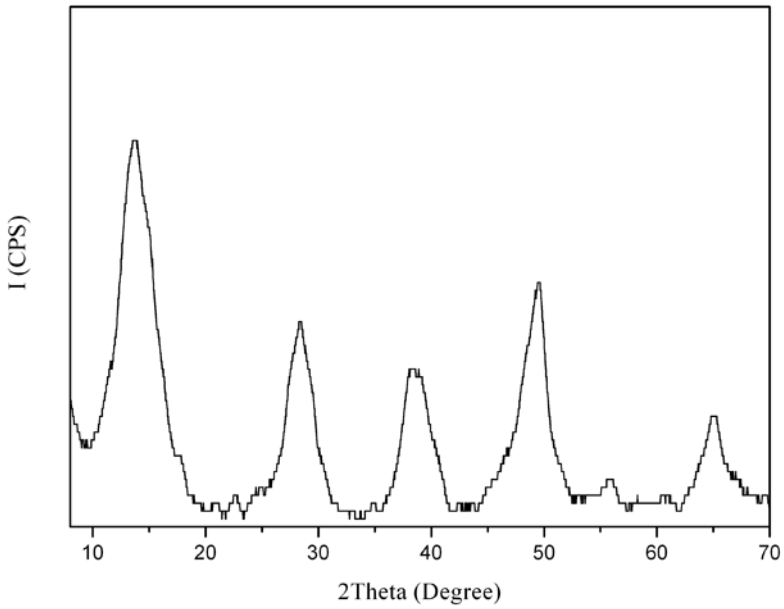

Fig. S1 Powder XRD pattern of the AlOOH sample.

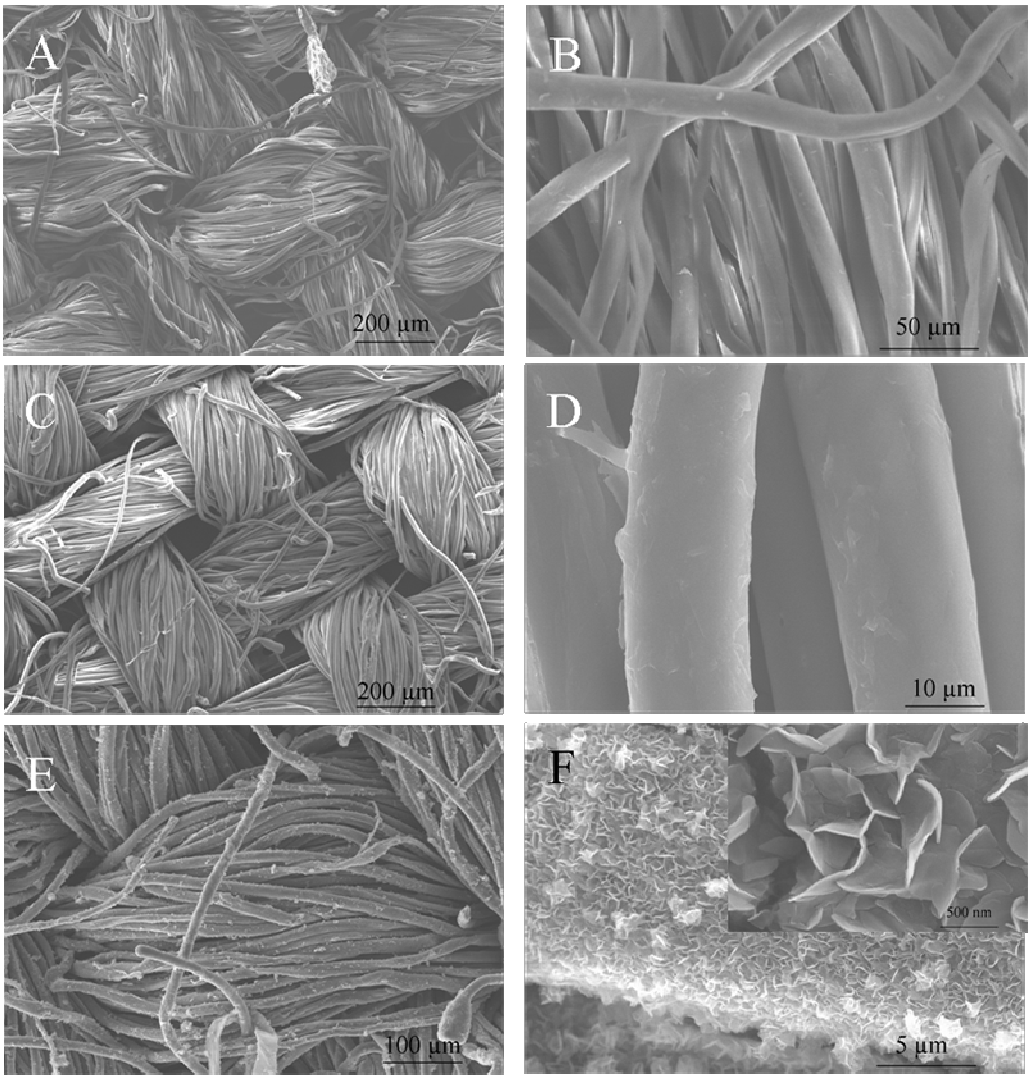

Fig. S2 SEM images of cloth at (A) low magnification and (B) high magnification; the cloth with 40 deposition cycles of boehmite coating at (C) low magnification and (D) high magnification; the ZnAl-LDH/cloth film at (E) low magnification and (F) high magnification.

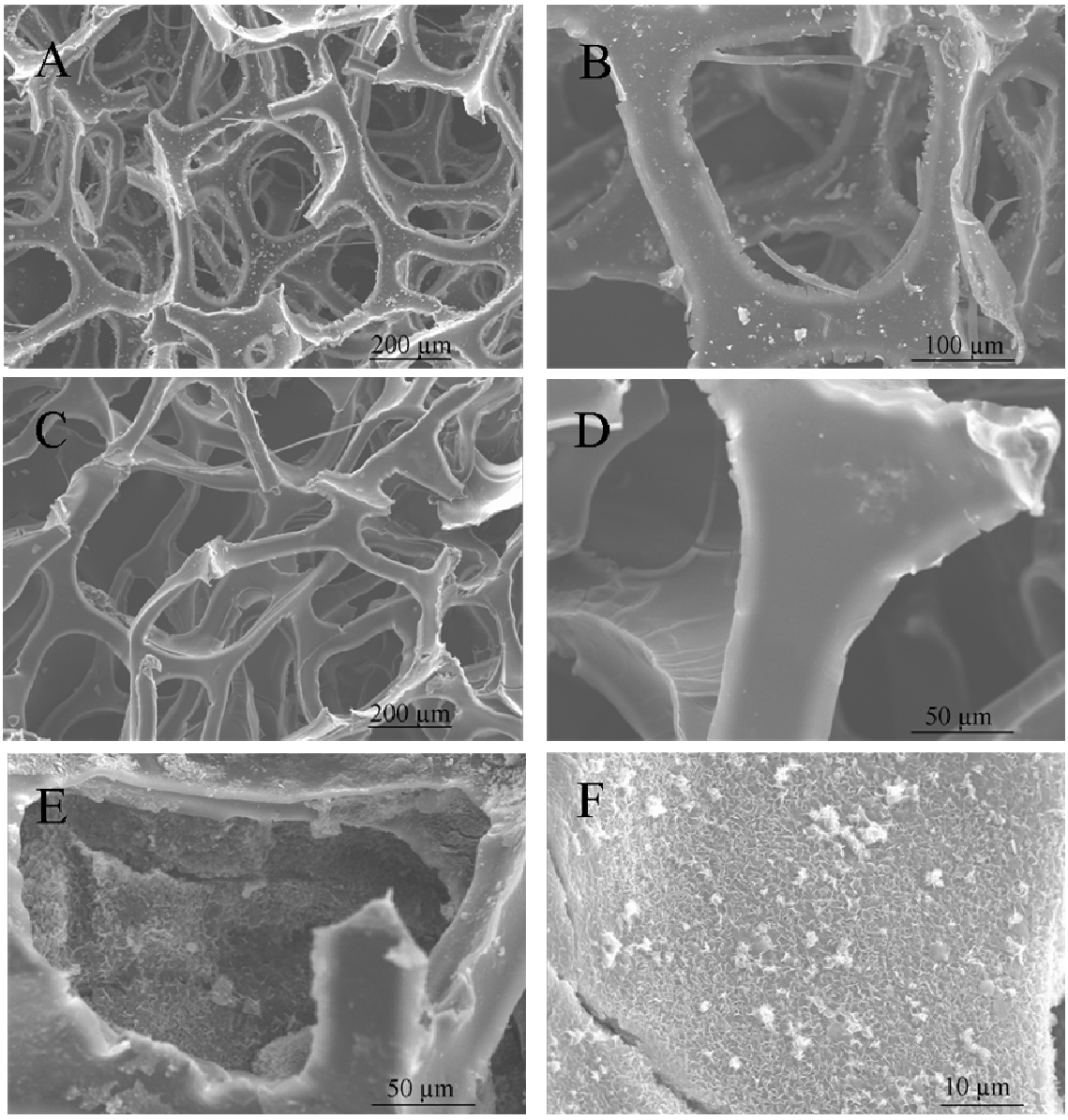

Fig. S3 SEM images of sponge at (A) low magnification and (B) high magnification; the sponge with 40 deposition cycles of boehmite coating at (C) low magnification and (D) high magnification; the ZnAl-LDH/sponge film at (E) low magnification and (F) high magnification.

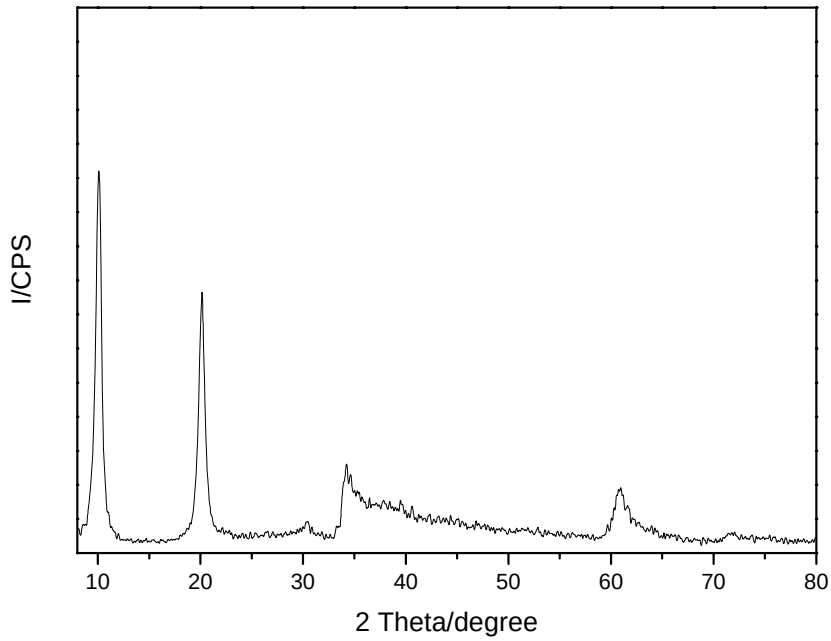

Fig. S4 Powder XRD pattern of the ZnAl-LDH powder sample.

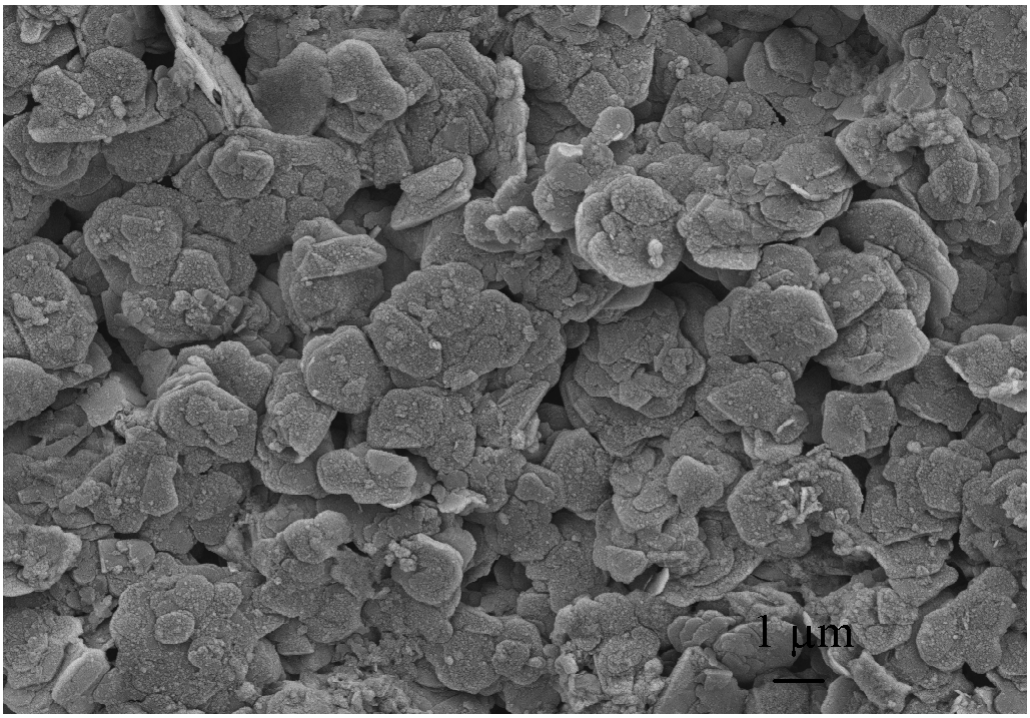

Fig. S5 SEM image of the ZnAl-LDH powder sample.

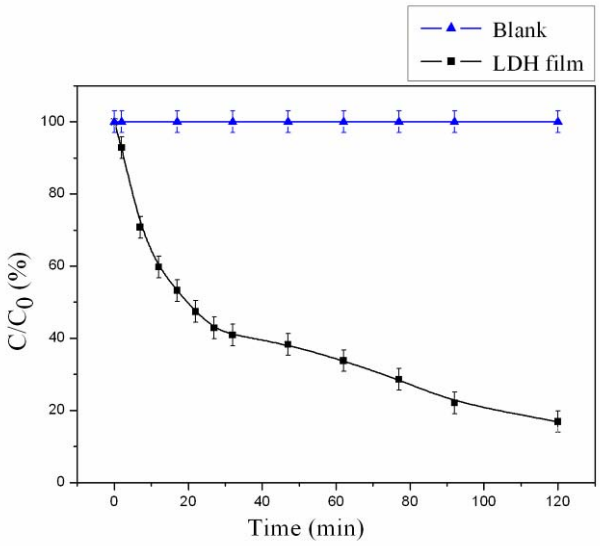

Fig. S6 Adsorption rate curves of $K_2Cr_2O_7$ (10 ppm) on the as-prepared ZnAl-LDH/paper film.

As shown in Fig. S6, there is no any self-adsorption of $K_2Cr_2O_7$ on the pristine paper, while the removal rate could reach ~ 84 % after 120 min. The adsorption capacity of the LDH film reaches to 2.0 mg/g.

References:

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2. Z. Lv, F. Z. Zhang, X. X. Lei, L. Yang, S. L. Xu and X. Duan, *Chem. Eng. Sci.*, 2008, **63**, 4055.

3. X. L. Liu,. M. Wei, Z. L. Wang, D. G. Evans and X.Duan, *J. Phys. Chem. C*, 2008, **112**, 17517.