Electronic Supplementary Information

Highly Oriented Nanoplates of Layered Double Hydroxides as a Ultra Slow Release System

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Experimental

Preparation of LDH-AQS: For synthesis of MgAl-LDH-AQS, 0.20 M of MgCl₂·6H₂O, 0.10 M of AlCl₃·9H₂O, 0.15 M of anthraquinone-2-sulfonic acid sodium salt and 0.35 M of hexamethylenetetramine were dissolved in 30 mL of deionized water. The mixture was put into a Teflon-leaned stainless steel autoclave, and then maintained at 180 °C for 48h. After the reaction was complete, the solid product was collected by filtration, washed with deionized water and acetone and dried at 70 °C.

Characterizations: X-ray diffraction (XRD) pattern was measured both on powder and films smaples with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in the $\theta \sim 2\theta$ scanning mode at 40 kV and 30 mA using Cu-K α radiation ($\lambda = 1.5405$ Å). The fourier-transform infrared spectroscopy (FT-IR) spectrum was recorded on a Biorad FTS 6000 FT-IR Spectrometer equipped with a high performance DuraSamplIR II diamond accessory with an attenuated total reflectance (ATR) mode in the range of 500–4000 cm⁻¹ with 100 scans at 4 cm⁻¹ resolution. The scanning electron microscopy (SEM) images were obtained on a JEOL 7401F (JEOL Ltd, Japan) operating at 30 kV. Before imaging, the samples were coated on carbon by sputtering with Pt to a thickness of about 3 nm. Transmission electron microscopy (TEM) images were taken on a JEOL 300KV (JEOL Ltd. Japan). The emission spectra were recorded on an Aminco-Bowman Series 2 Luminescence spectrometer equipped with a 150 W Xe lamp and a photon multiplier detector. Excitation wavelength of 280 nm was used and the emission spectra were recorded in the range of 450–750 nm.



Figure S1. XRD patterns and basal spacing (Å) of (a) LDH-AQS powder, (b) LDH-AQS thin film and (c) F-LDH-AQS thin film. The black circles correspond to the (*001*) harmonics for the basal spacings. The asterisk corresponds to the ITO peaks. The (b) and (c) for thin film samples also show the absence of (*101*) peak, meaning the high orientation of the LDH layers to the substrate plane.



Figure S2. (a) SEM image of microcrystalline MgAl-LDH-AQS, (b) schematic illustration for the interlayer structure of the MgAl-LDH-AQS, (c) exfoliated MgAl-LDH-AQS nanosheet colloid solution in formamide and (d) TEM image of the LDH nanosheet. Arrows indicate LDH nanosheets



Figure S3. FT-IR spectrum of (a) LDH-carbonate, (b) LDH-AQS film, and (c and d) F-LDH-AQS film. The large broadband centered at 3500 cm^{-1} is assigned to the overlapping stretching modes of hydroxyl groups present, those in both the brucite-type layer and the interlayer of water molecules. In (a), the peaks at 1361, 960 and 680 cm⁻¹ are ascribed to interlayer carbonate. In LDH-AQS film (b), the strong vibration band observed at around 1690 cm⁻¹ is assigned to the C=O stretching mode in AQS. The peaks at 1590, 1473, and 1413 cm⁻¹ are assigned to the C=C aromatic stretching mode and others at 1334 and 1300 cm⁻¹ to the C–H aromatic stretching modes in AQS. The peaks at 1213 (broad), 1176, and 1037 cm⁻¹ are attributed to the asymmetrical and symmetrical stretching modes of the interlayer sulfonate anion, respectively. In F-LDH-AQS film (c), the peaks at 1730 and 1376 cm⁻¹ are assigned to the C=O vibration and C–O vibration in cyclic ester of fluorescein dyes.



Figure S4. XRD patterns and basal spacing (Å) of (a) carbonate–LDH, (b) nitrate–LDH and (c) fluorescein–LDH. The asterisk corresponds to the (*001*) harmonics. In (b) and (c), no diffraction patterns assignable to carbonate phases were detected. The relative intensity of the first two (*001*) peaks in fluorescein– LDH was probably attributed to an increase in electron density in the mid-plane of the interlayers.[1,2]

References

- [1] P. Beaudot, M. E. de Roy, J. P. Besse, J. Solid State Chem., 2001. 161, 332–340.
- [2] P. Beaudot. M. E. de Roy, J. P. Besse, J. Solid State Chem., 2004. 177, 2691–2698.