Electronic Supporting information

Synthesis of ultrafine layered double hydroxides (LDHs) nanoparticles using a continuous-flow hydrothermal reactor

Qiang Wang,[a,b] Selina Tang,[c] Edward Lester,[c,d] Dermot O'Hare[*,b]

[a] College of Environmental Science and Engineering, Beijing Forestry University, Qinghua East Road, Haidian District, Beijing 100083, P. R. China

[b] Chemistry Research Laboratory, Department of Chemistry, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, UK

[c] Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

[d] Promethean Particles Ltd, Biocity, Nottingham, NG1 1GF, UK

Contents

1. Synthesis of LDHs

In the synthesis, the metal precursor solutions were prepared by dissolving 9.6 g $Mg(NO_3)_2{\cdot}6H_2O$ and 4.7 g $Al(NO_3)_3{\cdot}9H_2O$ or 8.85 g $Ca(NO_3)_2{\cdot}4H_2O$ and 4.7 g $Al(NO_3)_3{\cdot}9H_2O$ in 500 ml DI water, and the base solutions were prepared by dissolving 5.12 g NaOH and 2.65 g Na_2CO_3 or 5.12 g NaOH and 2.125 g $NaNO_3$ in 1000 ml DI water. The continuous flow Nozzle reactor used in this work has been previously described in detail and the animated image is shown in Figure 1. For the synthesis of $Mg_3Al\text{-}CO_3$ LDH, the base aqueous solution containing NaOH and Na_2CO_3 was pumped (20 ml/min) through the pre-heater before flowing into the inner tube (down-flow) of the Nozzle reactor. Simultaneously, the metal precursor aqueous solution containing $Mg(NO_3)_2$ and $Al(NO_3)_3$ was pumped (10 ml/min) at ambient temperature into the reactor (up-flow), to meet the down-flow. For the synthesis of $Ca_2Al\text{-}NO_3$ LDH, the base aqueous solution containing NaOH and $NaNO_3$ and the metal precursor aqueous solution containing $Ca(NO_3)_2$ and $Al(NO_3)_3$ were used instead. The retention time for all synthesis was adjusted to ca. 4 s. A matrix of samples was created by employing four different reaction temperatures, and two different system pressures; the pre-heater was set at 75, 150, 250 or 400 ^oC while the system pressure was maintained at 50 or 240 bar by the back pressure regulator. The products were immediately cooled down using cooling water.

2. Characterisation

X-ray diffraction (XRD) – XRD patterns were recorded on a PANalytical X'Pert Pro instrument in reflection mode with Cu Ka radiation. The accelerating voltage was set at 40 kV with 40 mA current (λ = 1.542A°) at $0.01^o\ s^{-1}$ from 5^o to 70^o with a slit size of 1/4 degree.

Transmission Electron Microscopy (TEM) – TEM analysis was performed on JEOL 2100 microscope with an accelerating voltage of 400 kV. LDH nanoparticles were dispersed in water with sonication and then cast onto copper grids coated with Formvar film.

Scanning Electron Microscopy - Energy Dispersive X-ray analysis (SEM-EDX) – The chemical composition of synthesised LDHs was determined by SEM-EDX analysis, which was performed on a JEOL JSM 6100 scanning electron microscope with an accelerating voltage of 20 kV. LDHs powders were spread on carbon tape adhered to an SEM stage.

Atomic Force Microscopy (AFM) – LDH suspensions in water were deposited onto freshly cleaved highly oriented pyrolytic graphite (HOPG, 10 ×10 × 2 mm from Agar) by spin-coating (2000 rpm, 30 s). AFM imaging was performed in tapping mode using a Nanoscope Multimode system (Digital Instruments, Santa Barbara, USA) with a Nanoscope IIIa controller and a "J" scanner having a lateral range of approximately 100 μm and a vertical range of 6 μm. The imaging was completed at room temperature and 30–50% relative humidity, with a silicon tip NST-NCHFR (Nascatec GmbH). Calibration of the AFM was accomplished by scanning a 10 μm pitch 200 nm 3D reference from Digital instruments.

Table S1. FWHM of 003 Bragg reflections and calculated crystallite size[$] of Ca_2Al-NO_3 and Mg_3Al-CO_3 for LDHs synthesised at different pressures and temperatures.

LDHs	Pressure (bar)	Temperature (^oC)	FWHM of 003 Bragg reflection	Crystalite size (nm)
Ca_2Al-NO_3	50	75	0.13	62.1
	50	150	0.14	57.6
	240	150	0.21	38.4
	240	400	0.32	25.2
Mg_3Al-CO_3	50	75	0.86	9.4
	50	150	0.84	9.6
	50	250	0.71	11.4
	240	75	0.71	11.4
	240	150	0.9	9.0
	240	250	0.7	11.6
	240	400	0.75	10.8

[$] using the Scherrer equation

Table S2. Ca/Al or Mg/Al ratio of $Ca_2Al\text{-}NO_3$ and $Mg_3Al\text{-}CO_3$ LDHs synthesised at different pressures and temperatures.

LDHs	Pressure (bar)	Temperature (^oC)	Ca/Al or Mg/Al ratio
$Ca_2Al\text{-}NO_3$	50	75	1.60
	50	150	1.76
	50	250	1.28
	240	75	1.60
	240	150	1.80
	240	250	1.55
	240	400	1.06
$Mg_3Al\text{-}CO_3$	50	75	2.87
	50	150	2.88
	50	250	3.52
	240	75	2.81
	240	150	2.91
	240	250	3.12
	240	400	2.47

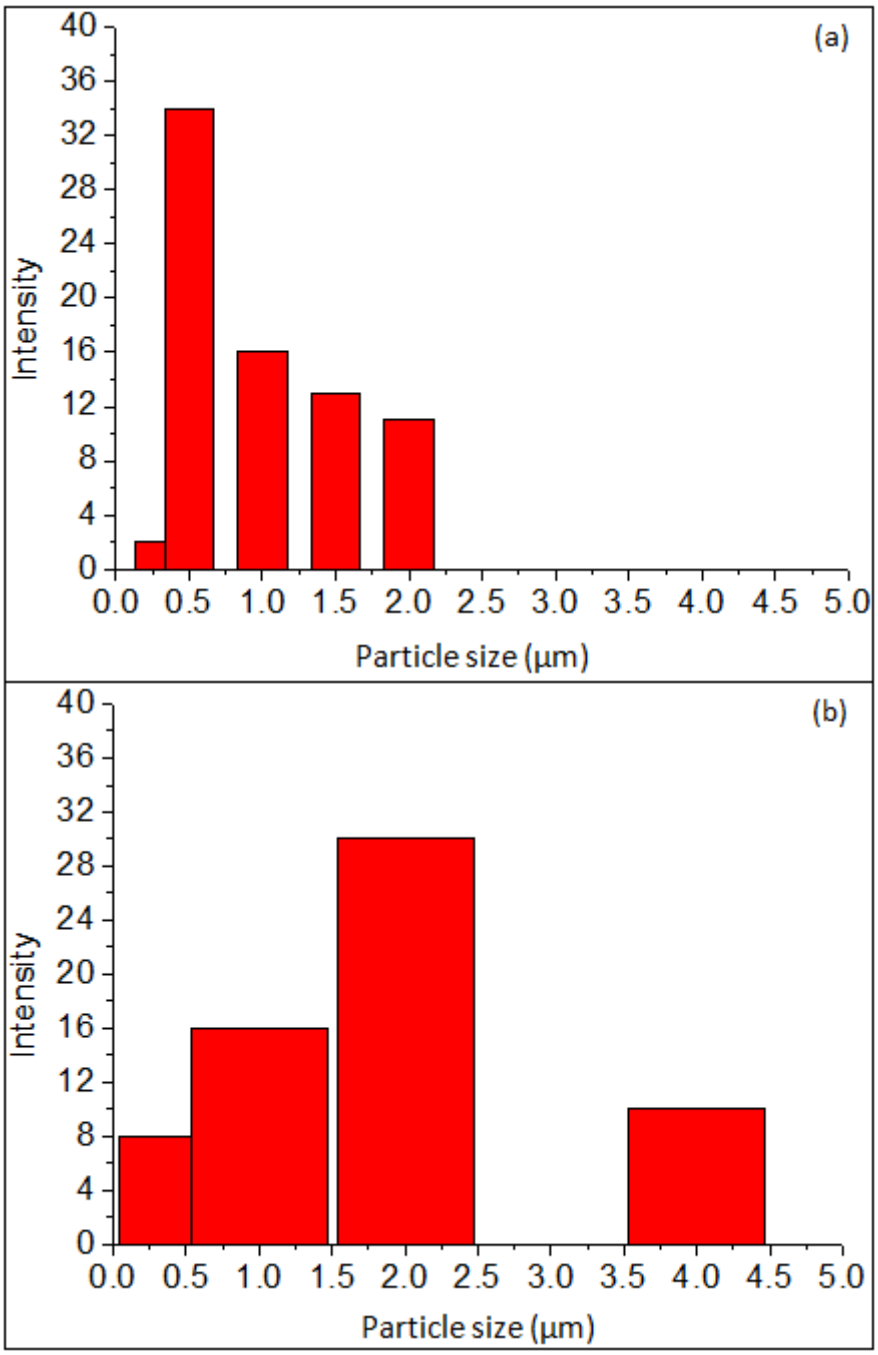

Figure S1. Particle size distribution of $Ca_2Al\text{-}NO_3$ LDH synthesized at (a) 50 bar and 75 ^{o}C, and (b) 50 bar and 150 ^{o}C.

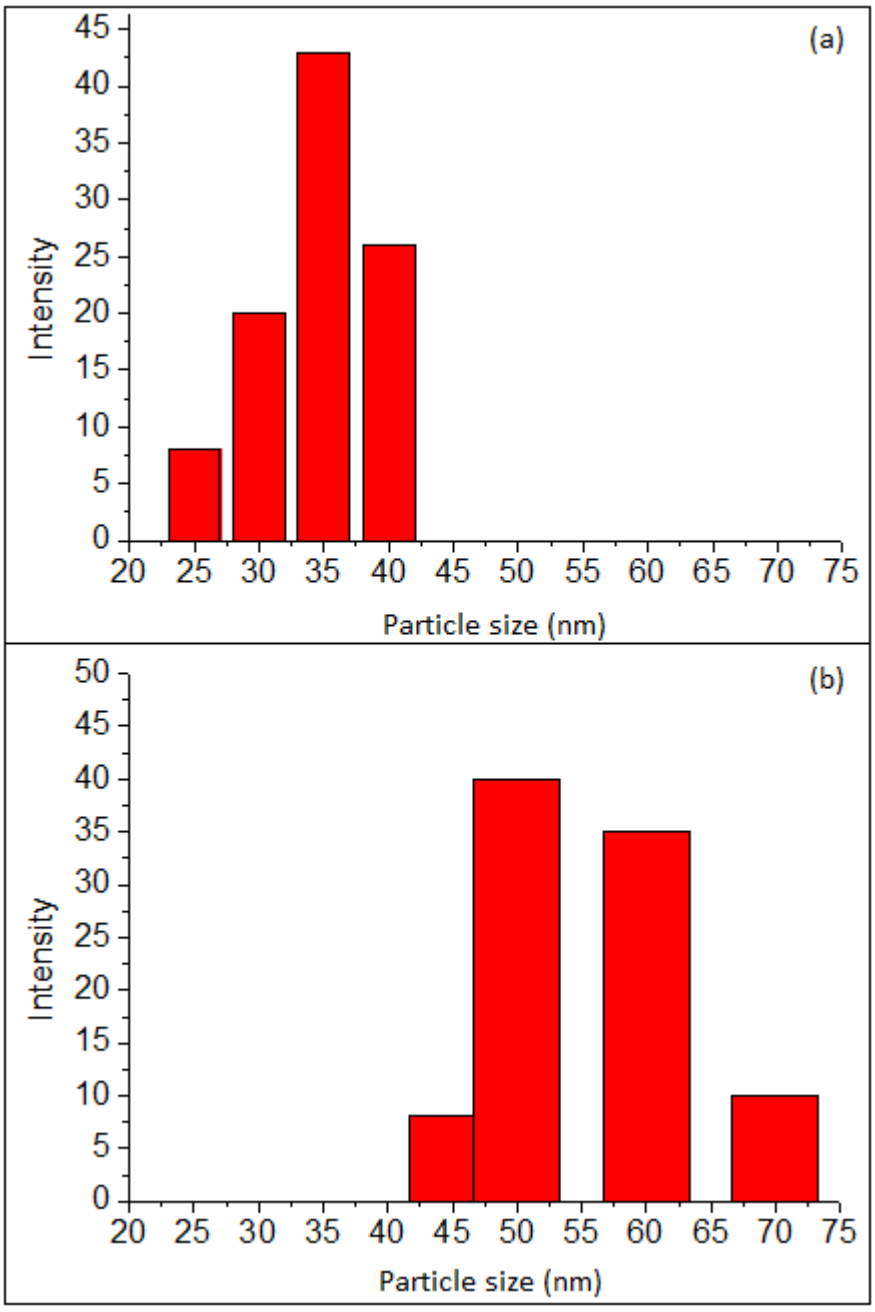

Figure S2. Particle size distribution of $Mg_3Al\text{-}NO_3$ LDH synthesized at (a) 50 bar and 75 ^{o}C, and (b) 50 bar and 150 ^{o}C.

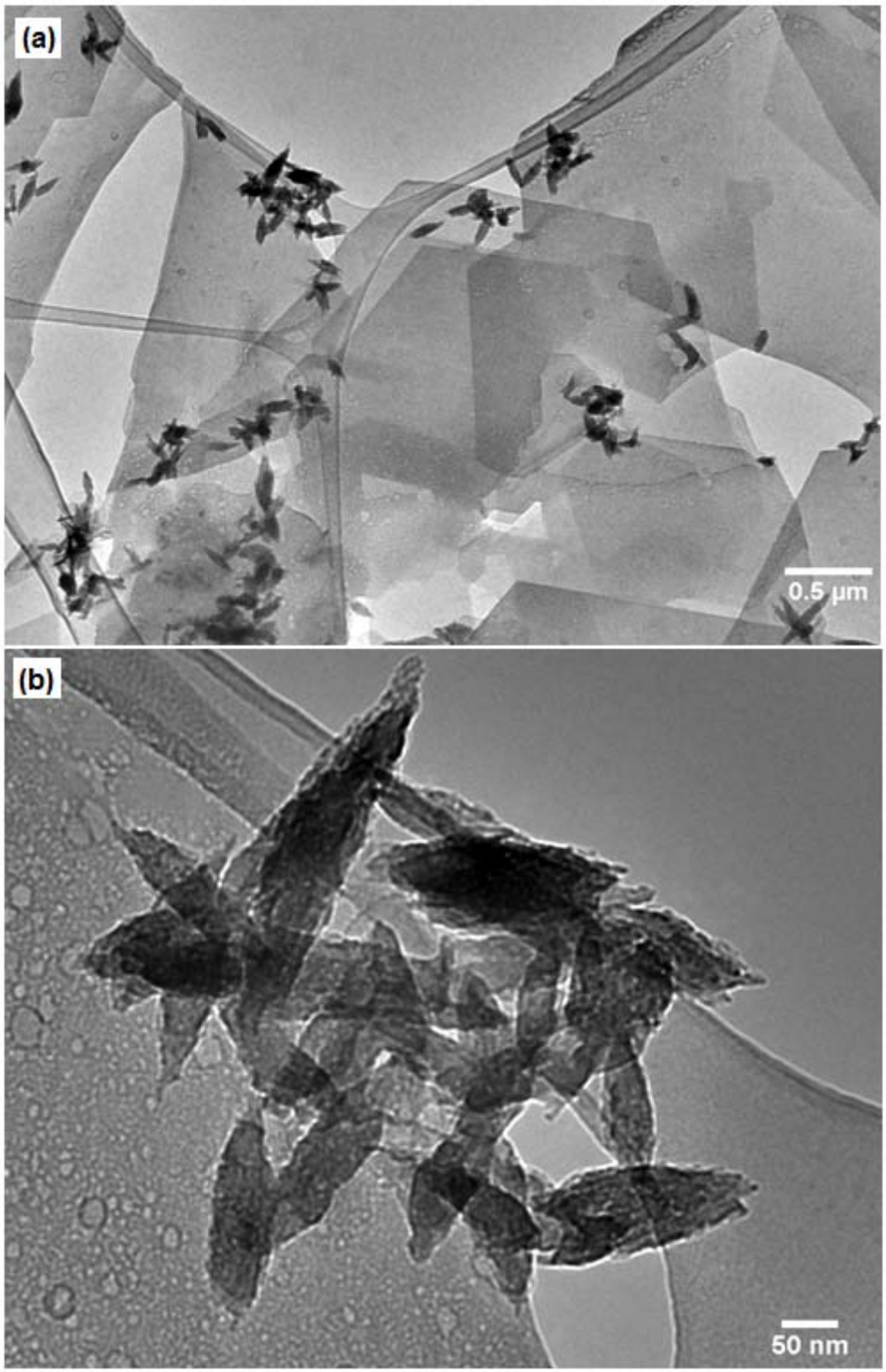

Figure S3. TEM images of $Ca_2Al\text{-}NO_3$ (50 bar, 150 ^{o}C) LDHs.

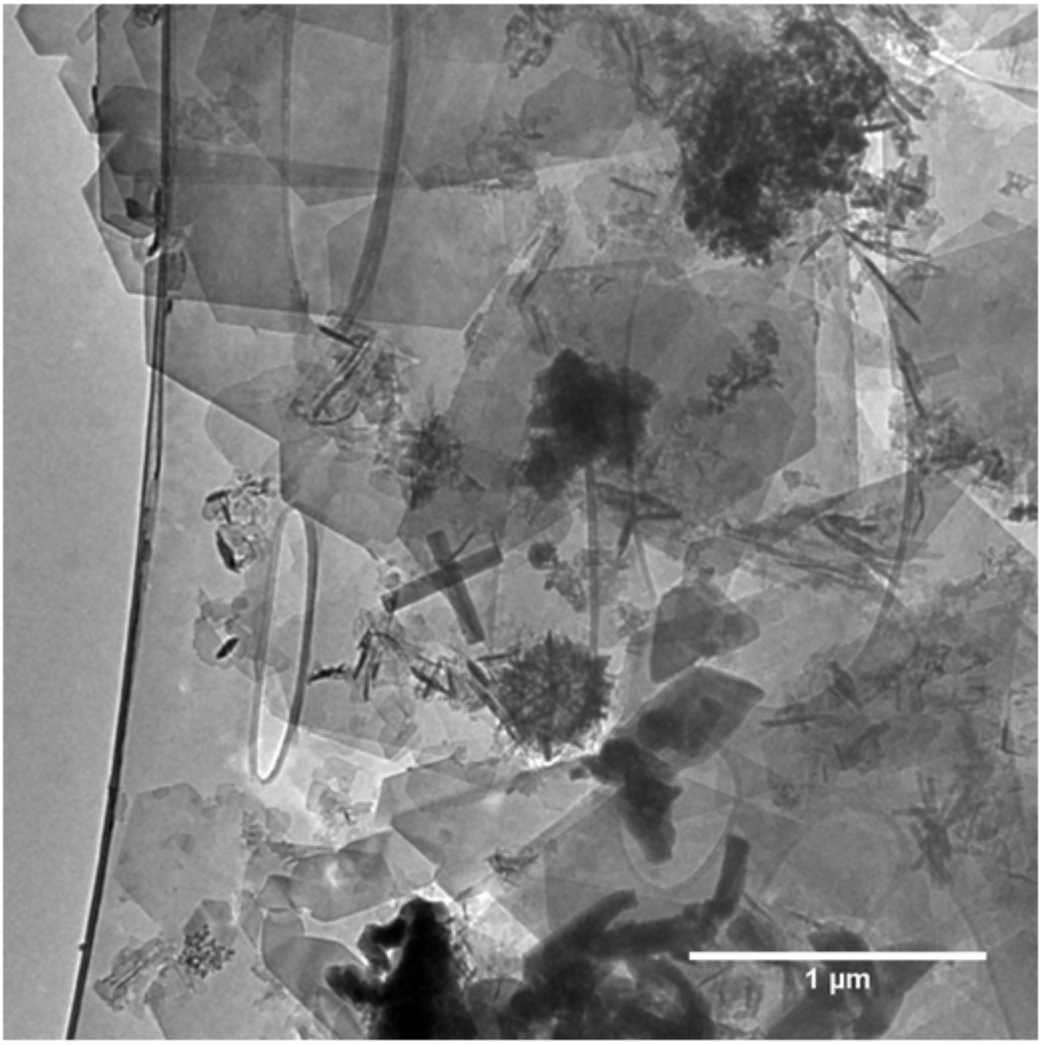

Figure S4. TEM image of $Ca_2Al\text{-}NO_3$ LDH synthesised at 240 bar and 400 ^{o}C.

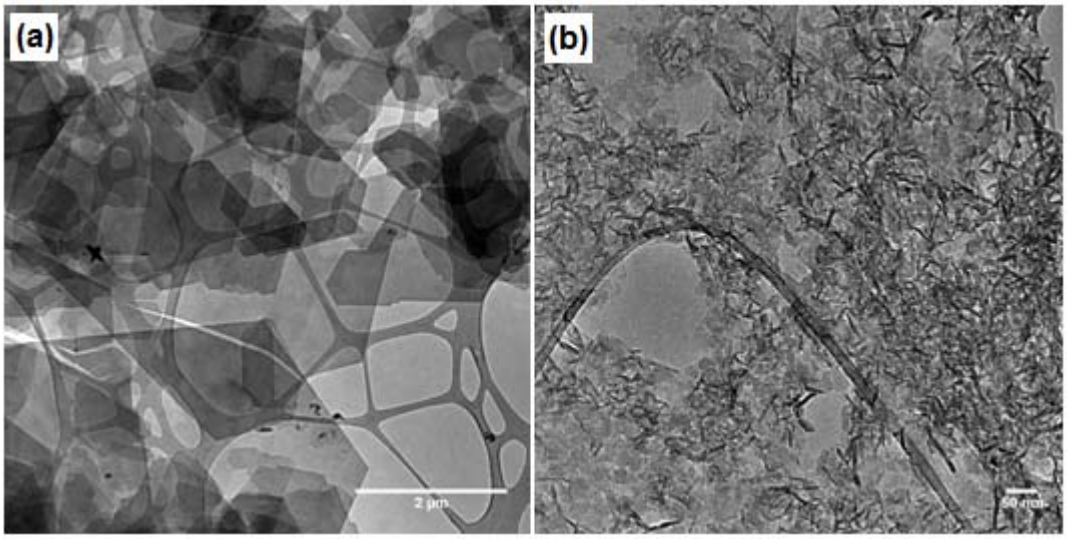

Figure S5. TEM images of (a) $Ca_2Al\text{-}NO_3$ (240 bar, 75 ^oC), and (b) $Mg_3Al\text{-}CO_3$ (240 bar, 75 ^oC) LDHs.