

Electronic Supplementary Information (ESI)

**Water adsorbancy of high surface area layered double hydroxides
(AMO-LDHs)**

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1. Experimental Part and characterisation

Experimental Part:

The detailed water vapor measurement procedures are shown as below: weight a clean and dry vial with cap, recorded as $M0$. 200 mg of sample was added into the vial and weight together with the vial and cap, recorded as $M1$. The vial containing sample (named as sample vial) without cap is put in the humidity box and the box is sealed. At certain time interval, the vial is taken out and closed with the cap immediately. Record the weight of the sample vial with cap, recorded as Mi . In order to compare samples fairly, the water vapor uptake of all the samples are based on dry basis. The water vapor uptake can be calculated by

$$\text{Water vapor uptake wt\% of dry LDH} = \frac{Mi - M1}{(M1 - M0) \times w}$$

w is the weight percentage of dry LDH obtained from TGA at 180 °C for $\text{Zn}_2\text{MgAl-CO}_3$ AMO-LDH and 200 °C for $\text{Mg}_3\text{Al-CO}_3$ AMO-LDH, at which the temperature the water molecules were released completely according to the 1st deviation curve derived from TGA results as shown in Fig. S1.

Characterisation:

Powder X-ray diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using Cu K α radiation ($\alpha_1 = 1.54057 \text{ \AA}$, $\alpha_2 = 1.54433 \text{ \AA}$, weighted average = 1.54178 \AA).

Thermogravimetric analyses (TGA) was carried out on a Mettler Toledo TGA/DSC 1 system. Samples (10 mg) were heated in an alumina crucible from 25 to 800 °C (at 5 °C min⁻¹) under N₂ flowing at 100 cm³ min⁻¹.

Specific surface areas and pore size were analysed using the Brunauer–Emmett–Teller (BET) method. The samples were measured from the N₂ adsorption and desorption isotherms at 77 K collected from a Micromeritics TriStar II plus. Before each measurement, LDH samples were first degassed overnight at 110 °C.

The Fourier-transform Infrared (FTIR) spectra were recorded on a Vertex 80 Spectrometer. It is equipped with a high performance DuraSamp1IR II diamond accessory of attenuated total reflection (ATR) mode in the range of 400-4000 cm⁻¹.

The solid state NMR spectroscopy (²⁷Al) was recorded by Dr. Nicholas Rees (University of Oxford) on a Varian Chemagnetics CMX Infinity 200 (4.7 T). Samples were packed in 7.5 mm zirconia rotors. A double resonance MAS probe was used for all measurements and a

MAS rate of 15 kHz was used for ^{27}Al . ^{27}Al MAS NMR spectra were acquired with a single pulse excitation applied using a short pulse length (0.7 μs). Each spectrum resulted from 2000 scans separated by 1 s delay.

2. Supporting figures and tables

Table S1. Formulation information of samples and comparison of C, H, H₂O+ethanol and mix metal oxide composition (wt%) in samples, estimated from formula and determined from experimental results.

Sample 1	Formula	
AMO-Mg ₃ Al-CO ₃	[Mg _{0.75} Al _{0.25} (OH) ₂](CO ₃) _{0.125} .0.5(H ₂ O).0.04(ethanol) ³	
Element composition	Theoretical (wt% from formula)	Experimental (wt%)
C	3.2%	3.1% ¹
H	4.2%	3.9% ¹
H ₂ O+ethanol	14%	17.8% ²
Mix Metal oxide	56%	54% ²
Sample 2	Formula	
AMO-Zn ₂ MgAl-CO ₃	[Zn _{0.5} Mg _{0.25} Al _{0.25} (OH) ₂](CO ₃) _{0.125} .0.06(H ₂ O).0.031(ethanol) ³	
Element composition	Theoretical (wt% from formula)	Experimental (wt%)
C	2.5%	2.5% ¹
H	2.6%	2.6% ¹
H ₂ O+ethanol	2.8%	10% ²
Mix Metal oxide	71%	67% ²

¹Element composition is determined from elemental analysis.

²Element composition is determined from TGA.

³The metal ratios were the theoretical ratio from raw material.

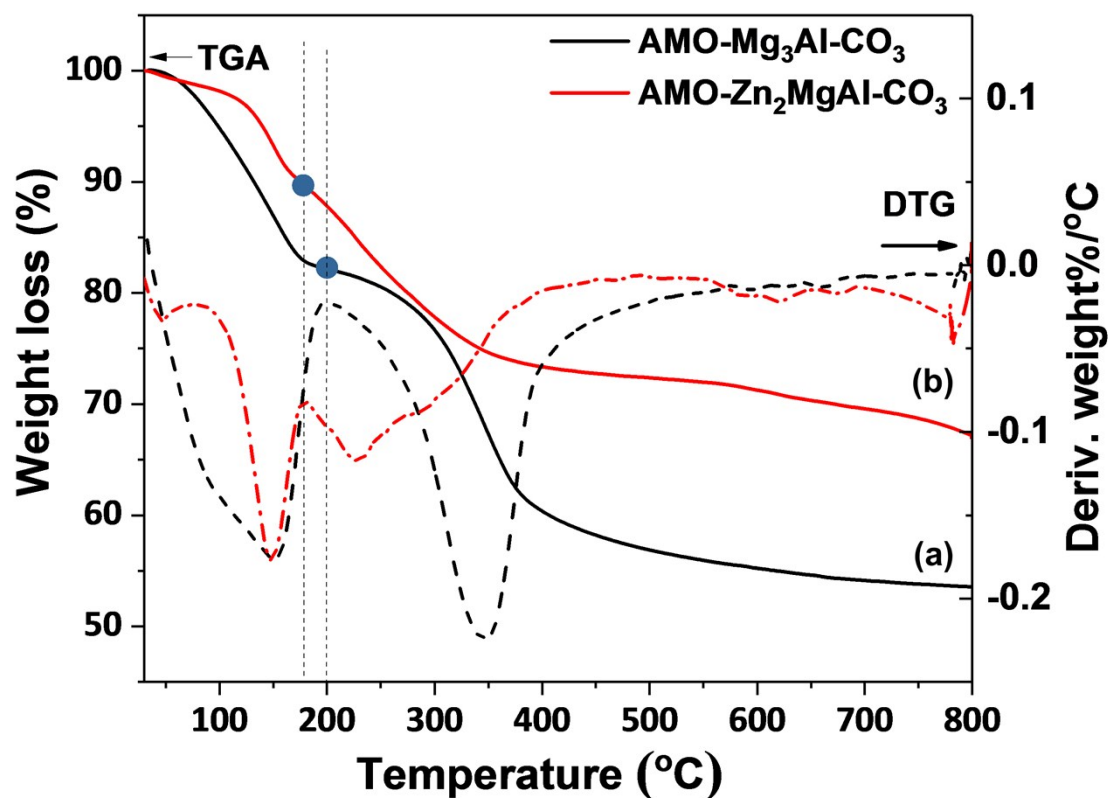


Fig. S1 TGA curves (solid lines) and 1st derivative curves (dashed lines) of (a) AMO-Mg₃Al-CO₃ and (b) AMO-Zn₂MgAl-CO₃.

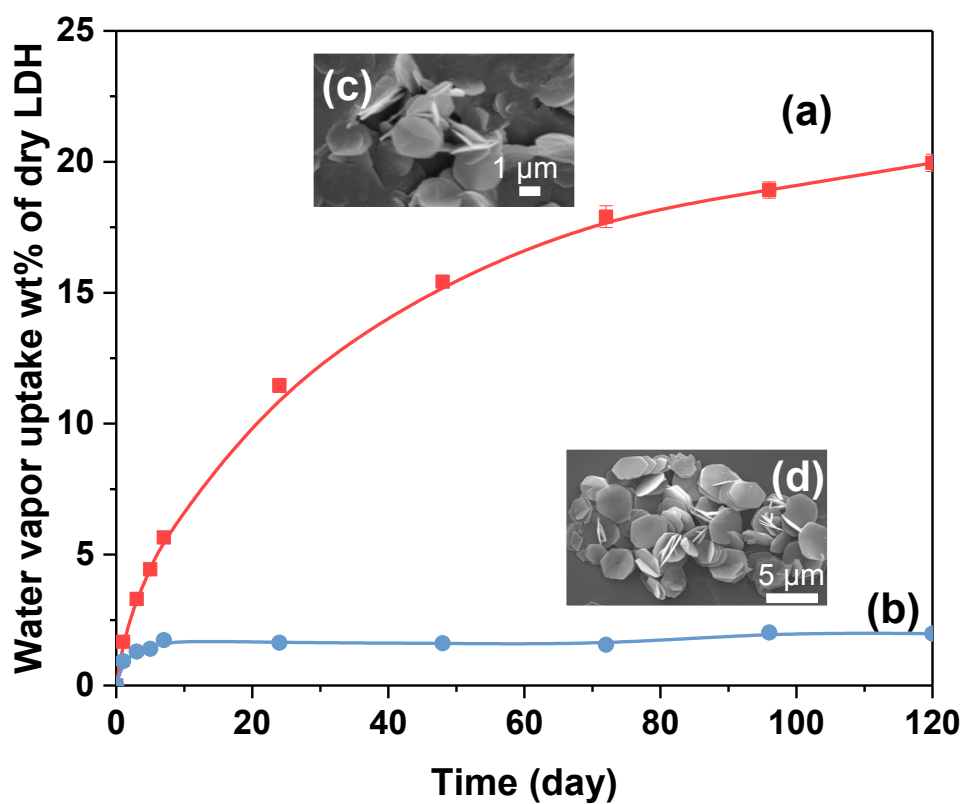


Fig. S2 Time dependence of water vapour uptake for LDH platelets with particle size of (a) 1-2 μm and (b) 4-5 μm; SEM images of LDH platelets with particle size of (c) 1-2 μm and (d) 4-5 μm.

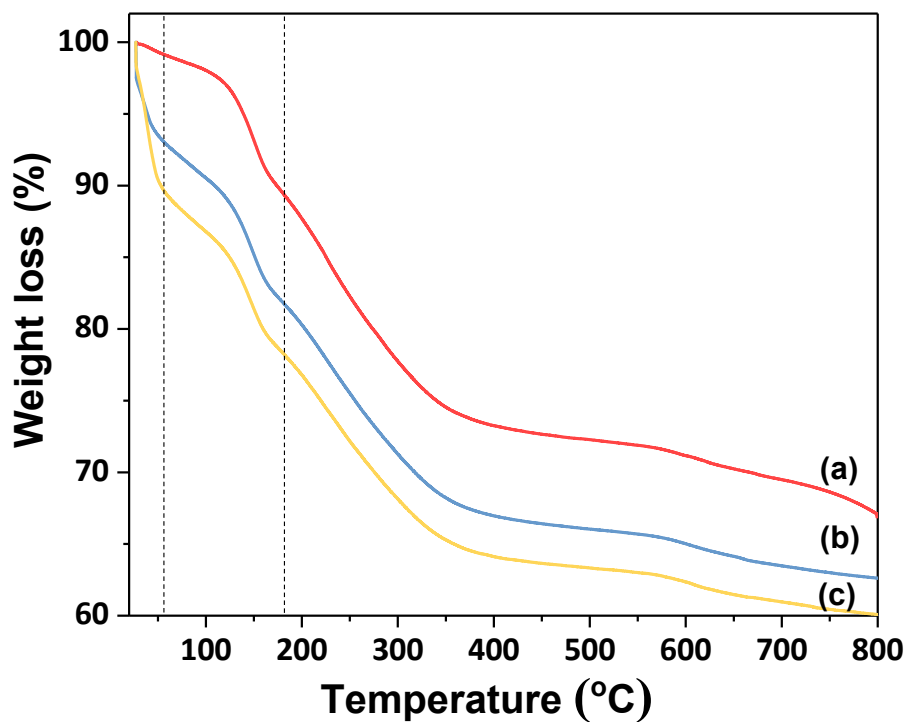


Fig. S3 TGA curves of AMO-Zn₂MgAl-CO₃ (a) before and after exposing in RH99 for (b) 24 h and (c) 72 h.

Table S2. Water content from TGA results and comparison with water vapor measurement result.

Sample	Interparticle pore water/AMO-solvent wt% of dry LDH (25-70°C)	Surface bond water wt% of dry LDH (70-180°C)	Ca. water vapor uptake wt% of dry LDH from TGA	Measured water vapor uptake wt% of dry LDH
Before RH99	1.2	10.5	0	0
RH99 24 h	9.5	12.7	10.5	11.3
RH99 72 h	14.6	13.1	16.0	17.7

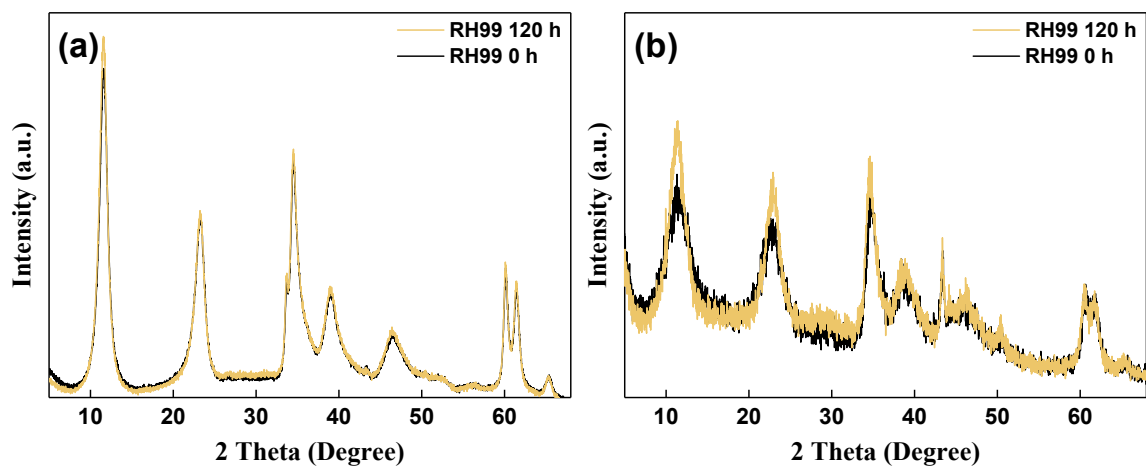


Fig. S4 XRD patterns of (a) AMO-Zn₂MgAl-CO₃ and (b) AMO-Mg₃Al-CO₃ before and after exposing in RH99 for 120 h

Table S3 The lattice parameters of AMO-LDH before and after exposing in RH99 at 20 °C

	Exposing time (h)	d spacing (Å)		Lattice parameter (Å) ¹	
		d(003)	d(110)	c	a
AMO-Zn₂MgAl-CO₃	0	7.63	1.54	22.9	3.07
	5	7.64	1.54	22.9	3.07
	24	7.65	1.54	22.9	3.07
	72	7.65	1.54	23.0	3.07
	120	7.66	1.54	23.0	3.07
AMO-Mg₃Al-CO₃	0	7.71	1.53	23.1	3.05
	120	7.80	1.53	23.4	3.05

¹ c is obtained from $c = 3 \times (003)$; a is obtained from $a = 2 \times (110)$.

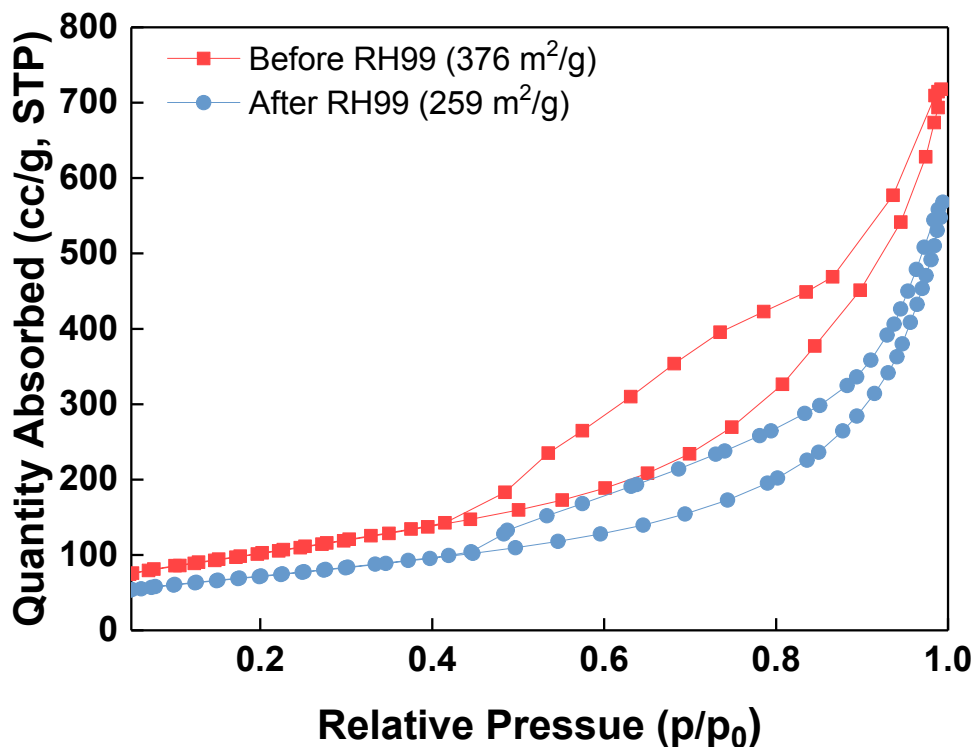


Fig. S5 N₂ adsorption and desorption isotherm curve of AMO-Mg₃Al-CO₃ LDH before and after exposing in RH99 for 120 h.

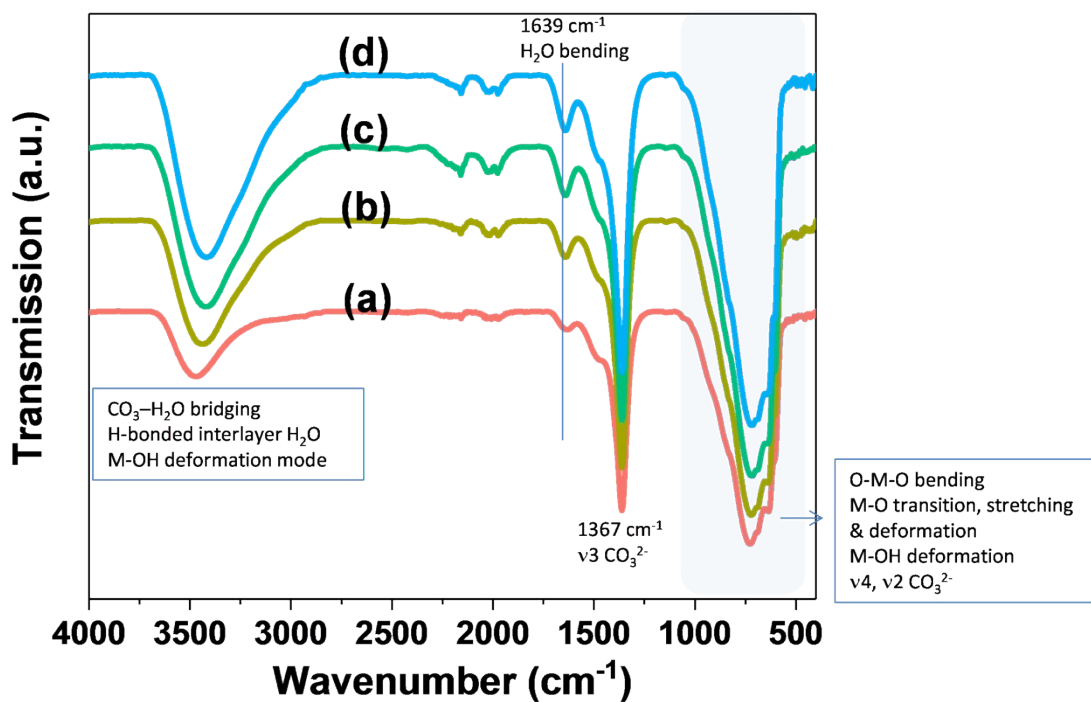


Fig. S6 FTIR curves of AMO-Zn₂MgAl-CO₃ (a) before and after exposing in RH99 for (b) 24 h and (c) 72 h

and (d) 120 h.

Table S4 Stearic acid loading in different samples.

Sample	Input (wt%)	Grafted SA* (wt%)
ZMA-SA0.25	7	5
ZMA-SA0.5	14	9
ZMA-SA1.0	28	11
ZMA-SA2.0	57	27

* Grated SA was calculated from TGA results of all samples without thermal treatment at 150 °C.

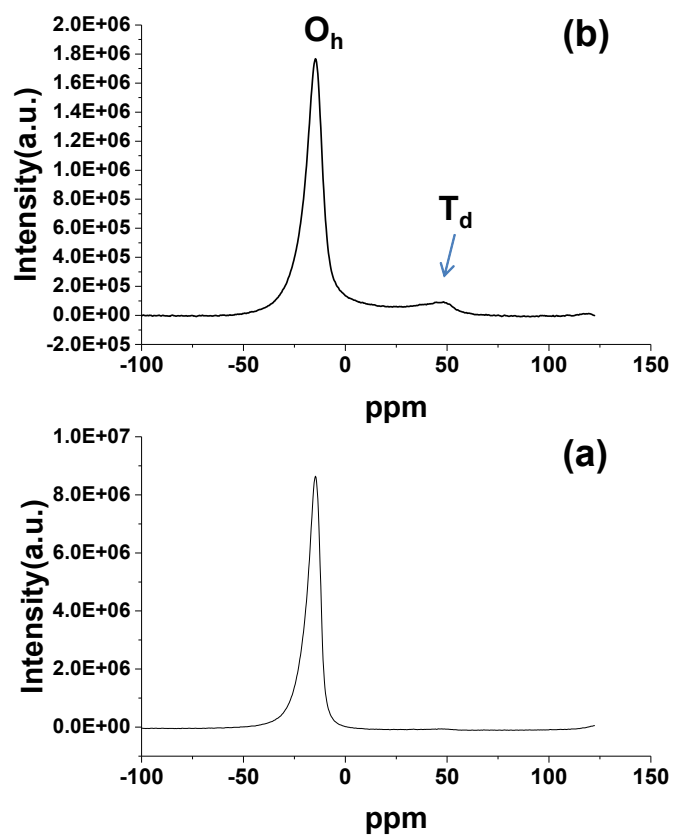


Fig. S7 ^{27}Al NMR of (a) $\text{AMO-Zn}_2\text{MgAl-CO}_3$ and (b) ZMA-SA0.25.

Table S5 Ratio of tetrahedral (Td) and octahedral (Oh) aluminum species in AMO-Zn₂MgAl-CO₃ and ZMA-SA0.25 from solid state ²⁷Al DPMAS NMR.

Sample	Al O _h /T _d ratio
AMO-Zn ₂ MgAl-CO ₃	100:0.5
ZMA-SA0.25	100:15

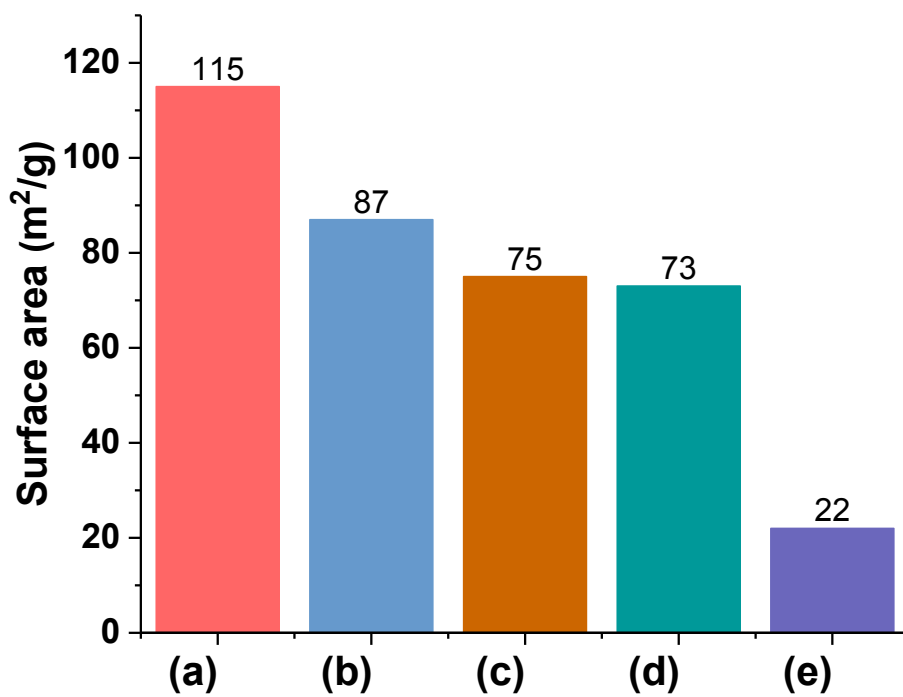


Fig. S8 BET surface area of (a) AMO-Zn₂MgAl-CO₃, (b) ZMA-SA0.25, (c) ZMA-SA0.5, (d) ZMA-SA1.0 and (e) ZMA-SA2.0.

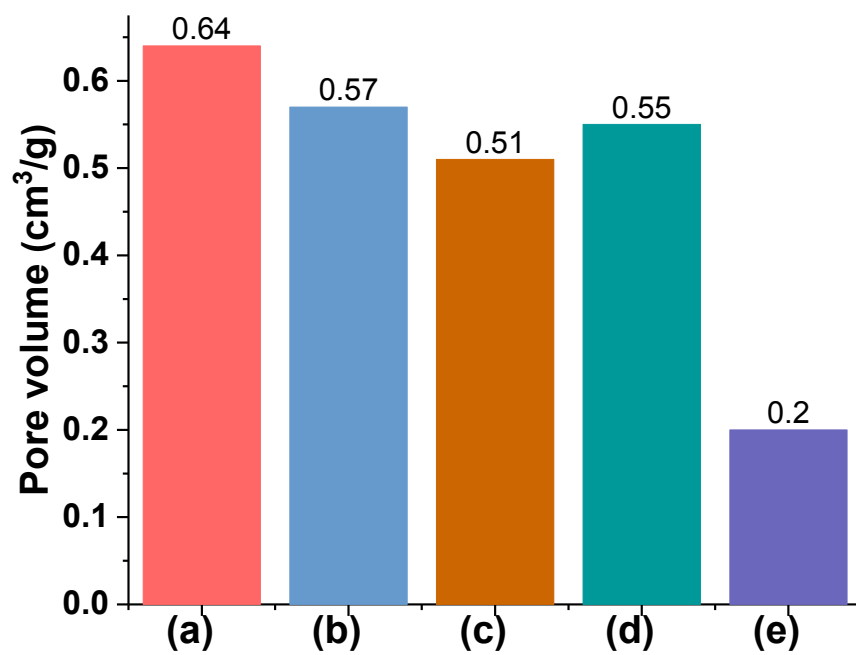


Fig. S9 Pore volume of (a) AMO-Zn₂MgAl-CO₃, (b) ZMA-SA0.25, (c) ZMA-SA0.5, (d) ZMA-SA1.0 and (e) ZMA-SA2.0.