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Supplementary Materials

Investigation of Thermal Behaviour of Layered Double Hydroxides Intercalated with Carboxymethylcellulose Aiming Bio-Carbon Based Nanocomposites

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Table S1. Interplanar distances d_{hkl} and 2θ (CuK_α) values from X-ray diffraction data of LDH-CO_3 and LDH-CMC. The indexation of diffraction peaks is based on R-3m space group.

hkl	Zn_2Al-CO_3		Mg_2Al-CO_3		Zn_2Al-CMC		Mg_2Al-CMC	
	2θ (°)	**d (nm)**	**2θ (°)**	**d (nm)**	**2θ (°)**	**d (nm)**	**2θ (°)**	**d (nm)**
(003)	11.729	0.754	11.570	0.765	3.543	2.492	5.047	1.750
(006)	23.562	0.378	23.290	0.382	6.156	1.435	10.578	0.836
(009)	35.809	0.251	--	--	10.130	0.873	--	--
(101)	33.968	0.264	--	--	--	--	--	--
(012)	34.675	0.259	34.905	0.257	33.930	0.264	35.270	0.254
(104)	37.379	0.241	--	--	--	--	--	--
(015)	39.300	0.229	39.406	0.229	--	--	--	--
(107)	44.078	0.205	--	--	--	--	--	--
(018)	46.866	0.194	46.788	0.194	--	--	--	--
(00$\underline{12}$)	48.145	0.189	--	--	--	--	--	--
(10$\underline{10}$)	53.090	0.172	52.899	0.173	--	--	--	--
(01$\underline{11}$)	56.491	0.163	56.242	0.164	--	--	--	--
(110)	60.306	0.153	60.853	0.152	60.547	0.153	61.208	0.151
(113)	61.663	0.150	62.161	0.149	--	--	--	--
(10$\underline{13}$)	63.823	0.146	63.395	0.147	--	--	--	--
(116)	65.645	0.142	66.054	0.141	--	--	--	--
(01$\underline{14}$)	67.751	0.138	--	--	--	--	--	--
d_{003} (nm)	0.754		0.765		2.492		1.750	
c (nm) *	2.262		2.295		7.476		5.250	
a and *b* (nm)	0.306		0.304		0.306		0.302	

(*) *c* parameter was calculated considering $c = 3 \times d_{003}$; (#) *a*/*b* parameter was calculated considering $a = 2 \times d_{110}$.

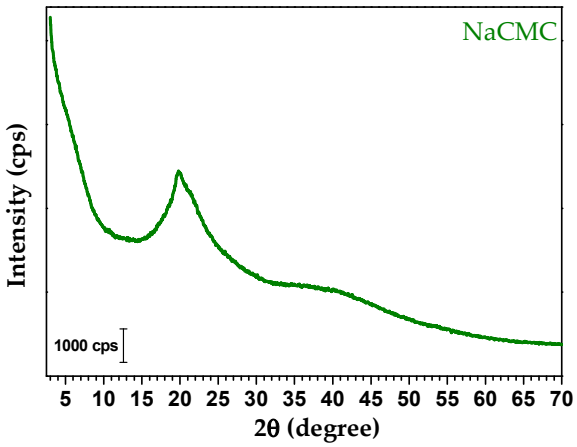

Figure S1. XRD pattern of sodium carboxymethylcellulose (NaCMC).

FTIR-ATR and Raman Spectra of LDH-CO_3 Samples

The infrared spectra of Zn_2Al-CO_3 and Mg_2Al-CO_3 are presented in Figure 4 in the main text. The broad band in the region between 3700–3100 cm^{-1} can be attributed to the stretching vibrations of the hydroxyl groups (νOH) from inorganic layer and the water molecules hydrogen-bonded. The shoulder at 3020 cm^{-1} region is assigned to νOH of H_2O molecules interacting with CO_3^{2-} by hydrogen bonding while the band at 1600–1635 cm^{-1} is related to the in-plane bending vibration of H_2O [1–4]. The bands of carbonate ions are observed in the region of 1354 cm^{-1} (antisymmetric stretching, ν_3), 860 cm^{-1} (out of plane, ν_2) and 680 cm^{-1} (in-plane bending, ν_4) [1,4,5]. In the region below 1000 cm^{-1}, the spectra show bands attributed to the lattice vibrations modes of the groups M-O-M and HO-M-OH (M = Zn^{2+}, Mg^{2+}, Al^{3+}). The strong band at 760 cm^{-1} is attributed to antisymmetric bending vibrations of HO-Al-OH groups [3,6] while the band at 674 cm^{-1}, only observed in Mg_2Al-CO_3 spectrum, can be attributed to antisymmetric bending of HO-Mg-OH groups.

FT-Raman spectra of Zn_2Al-CO_3 and Mg_2Al-CO_3 are also presented in Figure 4 in the main text. The broad band in the 3140 cm^{-1} region is attributed to the stretching vibrations of the layer hydroxide ions (νOH) and the H_2O molecules. The band at 1060 cm^{-1} is assigned to symmetric stretching (ν_1) of carbonate anion [1,5]. The band at 495 cm^{-1} is attributed to the antisymmetric stretching lattice of M^{2+}-O-Al [3] and shown to be dependent of M^{2+} cation, being more intense to Zn^{2+} possibly owing to its higher polarizability than Mg^{2+}. A tentative attribution of the main vibrational bands is presented in Table S2.

Table S2. Vibrational data of $Zn_2Al\text{-}CO_3$ and $Mg_2Al\text{-}CO_3$ samples.

$Zn_2Al\text{-}CO_3$		$Mg_2Al\text{-}CO_3$		Tentative Attribution	Reference
FTIR	Raman	FTIR	Raman		
3700–3100	3143	3700–3100	3143	νOH (M-OH and H_2O)	[1–4]
3026 (sh)	--	3026 (sh)	--	νOH (H_2O---CO_3^{2-})	
1400(sh)	--	1400(sh)	--	$\nu_3CO_3^{2-}$	[1,4,5]
1351	--	1358	--	$\nu_3CO_3^{2-}$	
1632	--	1600	--	$\delta_{ip}H_2O$	[1–4]
1058	1060	1058	1059	$\nu_1CO_3^{2-}$	[1,4,5]
946 (sh)	--	946 (sh)	--	δAl-O-H	[6]
863 (sh)	--	863 (sh)	--	$\nu_2CO_3^{2-}$	[1,4,5]
760	--	760	--	δas(HO-Al-OH)$_l$	[3,6]
--	698	688 (sh)	698	$\nu_4CO_3^{2-}$	[1,4,5]
--	--	674	--	δas(HO-Mg-OH)$_l$	[3]
630	--	630 (sh)	--	δs(HO-Al-OH)$_l$	[3]
556	--	558	--	νas(M^{2+}-O-Al)$_L$	[3]
--	565	--	565	νs(M^{2+}-O-Al)$_L$	[3]
525	--	--	--	δas(HO-Zn^{2+}-OH)$_l$	[4]
	495	--	483	νs(M^{2+}-O-Al)$_L$	[3]
423	--	440 (sh)	--	δas(M^{2+}-O-Al)$_L$	[3]
--	155	--	151	δ(O-M^{2+}-O)	[7]

ν = stretching; δ = bending; s: symmetric; as: antisymmetric; ip: in plane; sh: shoulder; L: lattice; *l* = vibrations; M^{2+} = divalent cation; ν_1 = symmetric stretching; ν_3 = antisymmetric stretching; ν_2 = bending out of plane; ν_4 = bending in plane.

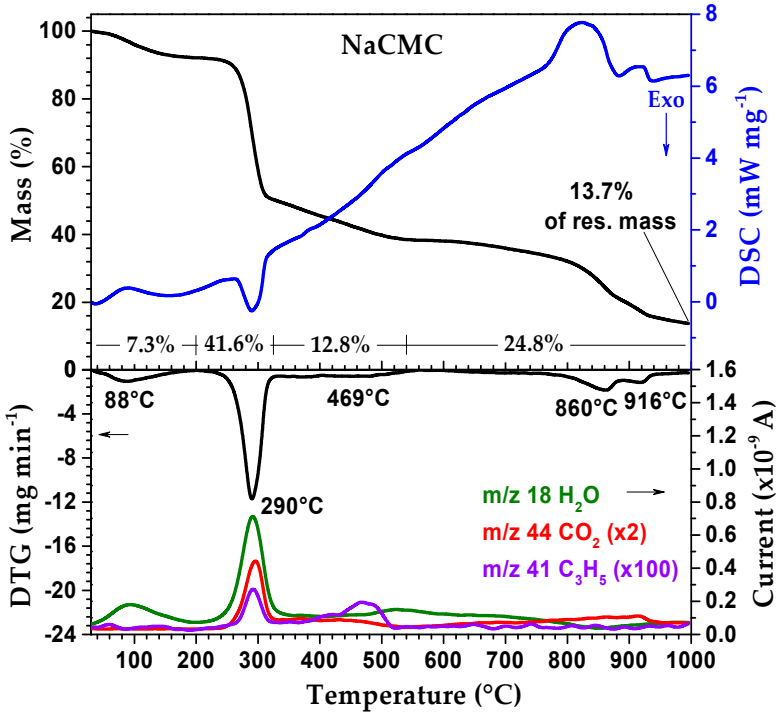

Figure S2. TG-DSC (up) and DTG-MS (down) curves of sodium carboxymethylcellulose (NaCMC) under N_2 atmosphere.

Table S3. Chemical analysis data and proposed formula for LDH-CO_3 and LDH-CMC samples.

Sample	Proposed Formula $^{\$}$	%C ^{ŧ}	%H_2O *
Mg_2Al-CO_3	$[Mg_{2.00}Al(OH)_{6.00}](CO_3)_{0.50}\cdot 2.43\ H_2O$	-- (2.39)	17.40 (17.40)
Zn_2Al-CO_3	$[Zn_{2.14}Al(OH)_{6.28}](CO_3)_{0.50}\cdot 3.28\ H_2O$	-- (1.66)	16.30 (16.30)
Mg_2Al-CMC	$[Mg_{2.18}Al(OH)_{6.36}](RU)_{1.15}(Cl)_{0.20}\cdot 2.36\ H_2O$	20.80 (20.90)	8.80 (8.68)
Zn_2Al-CMC	$[Zn_{1.84}Al(OH)_{5.68}](RU)_{1.43}(Na_{0.23}RU_{0.33})\cdot 2.88\ H_2O$	22.80 (22.80)	7.56 (7.56)

$^{\$}$ M^{2+}/Al^{3+} metal ratio was calculated from ICP OES; ^{ŧ} calculated from carbon elemental analysis; * calculated from TG curves; RU: $(C_6H_{10}O_5)(C_2H_2O_2)_{0.7}$; () values obtained based on the proposed formula.

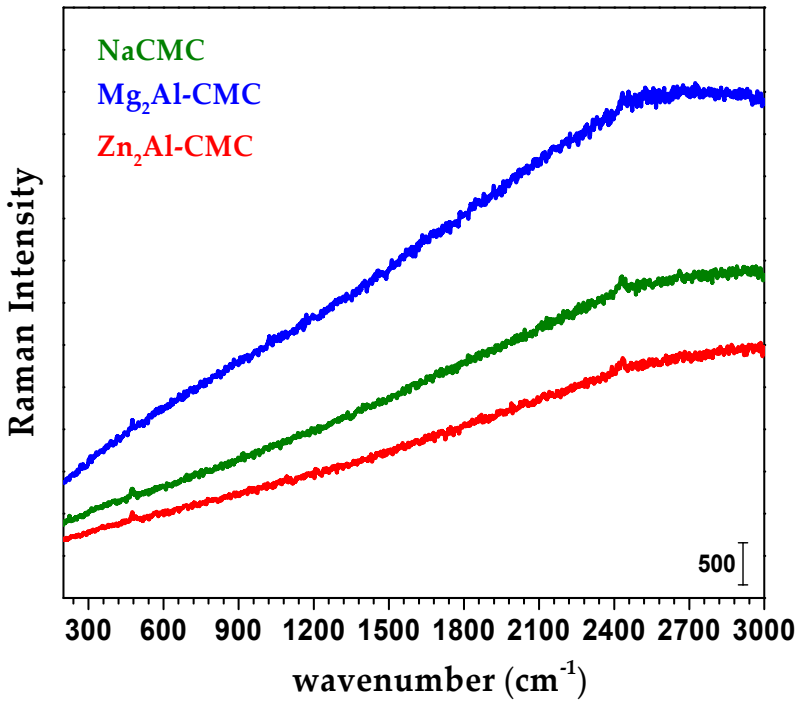

Figure S3. Raman spectra ($\lambda_{exc.}$ = 532 nm) of NaCMC and LDH-CMC samples.

FTIR-ATR Spectra of LDH-CO_3 Calcined Samples

FTIR-ATR spectra of calcined samples (MMO/C nanocomposites) are shown in Figure S4. LDH-CO_3 samples submitted to the same conditions than LDH-CMC materials were analysed by this vibrational technique for comparison. Zn_2Al-CO_3 sample heated at 500 °C presents two remarkable bands at 1532 cm^{-1} and 1388 cm^{-1} attributed to the split of ν_3 vibrational mode of carbonate anion. These vibrational bands present $\Delta\nu$ equal to 144 cm^{-1} and can be assigned to CO_3^{2-} ion coordinated to the layer metal cations [8]. Coordination process also activates the ν_1 mode of carbonate. The ν_3 bands are also noticed with low intensity in the spectrum of Zn_2Al-CO_3 calcined at 600 °C but are practically absent in FTIR-ATR spectra of samples calcined at 800 and 1000 °C. Hence, carbonate coordination to metal sites of LDH layers can explain the thermal profile observed above 500 °C for Zn_2Al-CO_3 sample (Figure 5 in the main text). Mg_2Al-CO_3 spectra also show bands at 1600–1350 cm^{-1} region but with different shape that can be attributed mainly to absorption of atmospheric carbon dioxide at high basic surface of calcined samples [9,10] (spectra were recorded in *ex situ* mode). In general, bands observed bellow 900 cm^{-1} are assigned to vibrational modes of M-O bonds, as presented in Table S2.

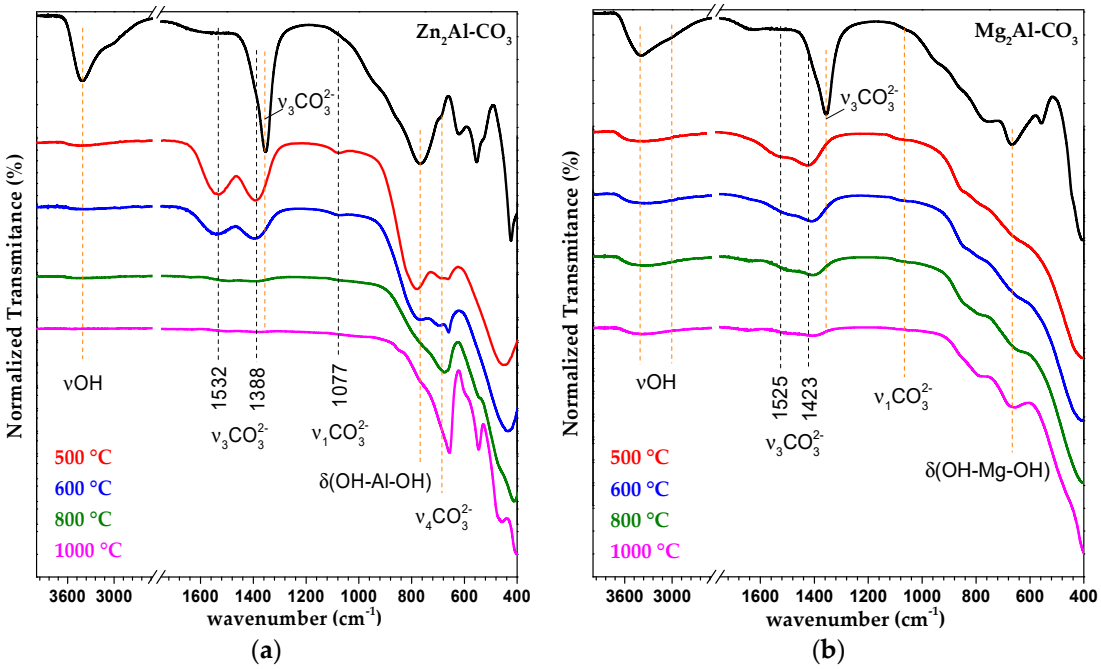

Figure S4. FTIR-ATR spectra of $Zn_2Al\text{-}CO_3$ (**a**) and $Mg_2Al\text{-}CO_3$ (**b**) samples calcined at 500, 600, 800 and 1000 °C under N_2 atmosphere.

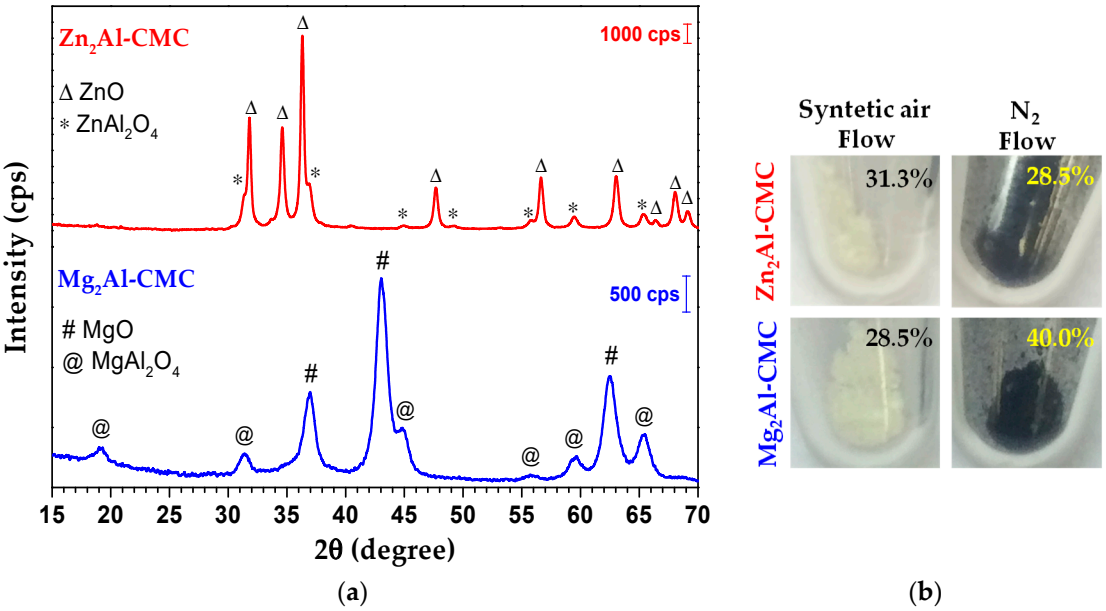

Figure S5. XRD patterns of $M_2Al\text{-}CMC$ samples calcined at 1000 °C under synthetic air (**a**). Pictures of $M_2Al\text{-}CMC$ samples calcined at 1000 °C under synthetic air or nitrogen atmosphere, indicating the percentage of residue after each heating process (**b**).

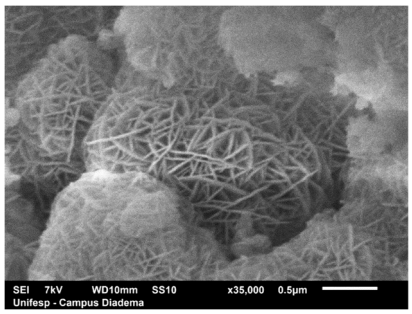

Figure S6. SEM image of $Mg_2Al\text{-}CO_3$ sample.

Thermodynamic Considerations about Carbothermic Reaction

Thermodynamic parameters were used to calculate the Gibbs free energy of carbothermic reaction ($\Delta_R G°$) between graphite carbon and metal oxides (ZnO and MgO). The standard molar thermodynamic parameters of each substance at 25 °C are shown in Table S4 and the results are presented in Table S5.

Table S4. Standard molar thermodynamic parameters of substances at 25 °C.

Substance	State	$\Delta_f H°$ kJ mol^{-1}	S° J K^{-1} mol^{-1}	$\Delta_f G°$ kJ mol^{-1}	Reference
$C_{(graf.)}$	s	0	5.74(10)	0	[11]
CO	g	−110.53(17)	197.660(4)	−137.16	[11]
ZnO	s	−348.280	43.64	−318.30	[12]
Zn^0	s	0	41.63(15)	0	-
	g	130.40(40)	160.990(4)	95.14	[11,12]
MgO	s	−601.6	26.95	−569.3	[11,12]
Mg^0	s	0	32.67(10)	0	-
	g	147.1(8)	148.648(3)	113.10	[11]

Table S5. Standard molar thermodynamic values for the carbothermic reaction between graphitic carbon and zinc or magnesium oxides at 25 °C. Values calculates from data presented in Table S4.

Chemical Equation of Reaction	$\Delta_R H°$ kJ mol^{-1}	$\Delta_R S°$ J K^{-1} mol^{-1}	$\Delta_R G°$ kJ mol^{-1}	T_{RS} (°C)	T_{exp} * (°C)
$ZnO_{(s)} + C_{(s)} \rightarrow Zn^0_{(v)} + CO_{(g)}$	368.15	309.26	276.29	917	>880
$MgO_{(s)} + C_{(s)} \rightarrow Mg^0_{(v)} + CO_{(g)}$	638.28	313.62	545.24	1762	-

T_{RS} = temperature of reaction spontaneity; * taken from the thermal analysis result (Figure 5).

Carbothermic reactions are obviously not spontaneous at 25 °C but the entropy ($\Delta_R S°$) is positive and the reactions tend to become spontaneous with increasing of the temperature. The value of temperature to promote a spontaneous carbothermic reaction (T_{RS}) was estimated considering that $\Delta_R H°$ and $\Delta_R S°$ do not change significantly and the equilibrium conditions. The calculated T_{RS} value suggests that carbothermic reaction for ZnO reduction tends to become spontaneous above 917 °C, a value very close to that one observed in this work (880 °C). For MgO, the T_{RS} value is much higher (1762 °C) than for ZnO. The results of calculations agree with the processes experimentally observed.

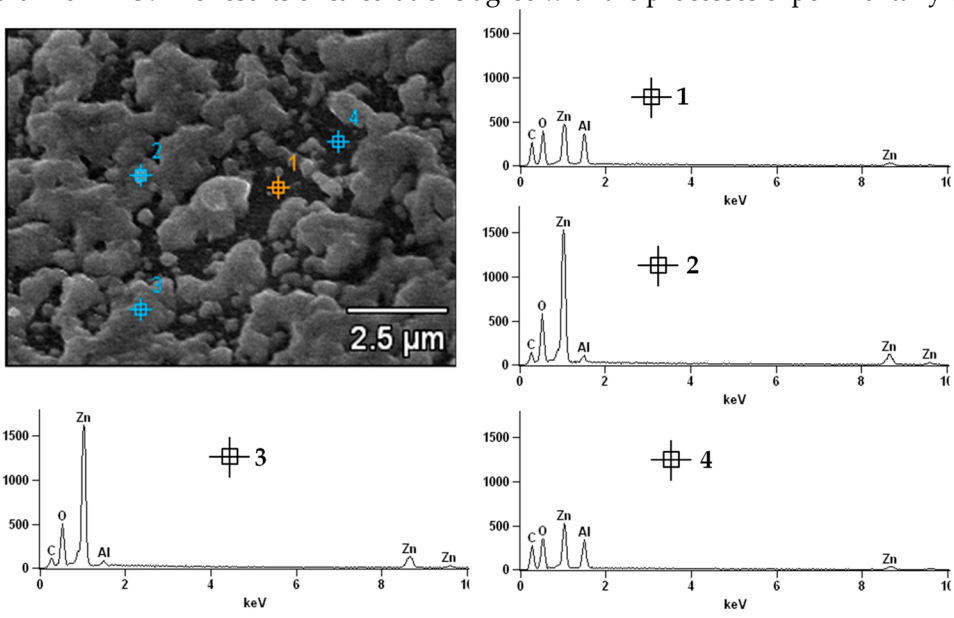

Figure S7. EDS spectra of Zn_2Al-CMC sample pyrolyzed at 800 °C.

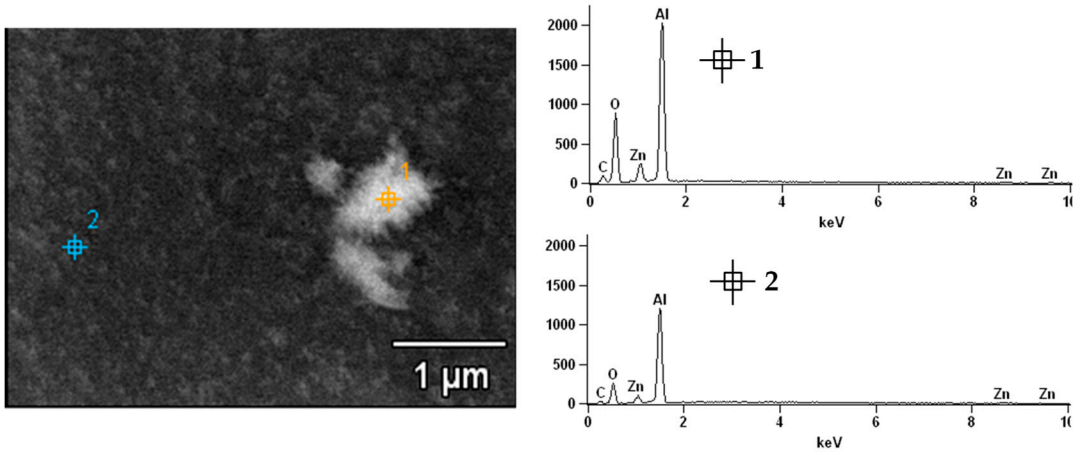

Figure S8. EDS spectra of Zn_2Al-CMC sample pyrolyzed at 1000 °C.

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