Supplementary Material

Study on the mechanism of morphology regulation of Pb-based MOFs and catalytic thermal decomposition mechanism of energy-containing materials

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Sample characterization

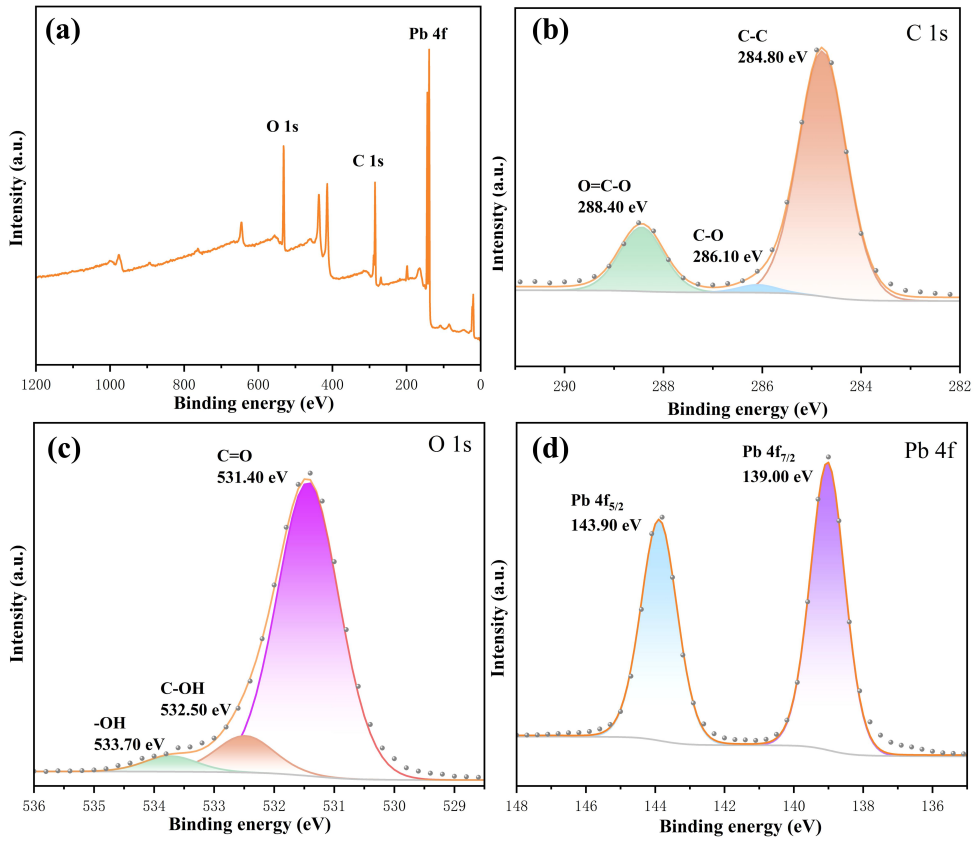

Fig. S1 XPS map of Pb-MOF-1, (a) full spectrum; (b) C 1s; (c) O 1s; (d) Pb 4f

As shown in Figure S1, the C 1s spectrum shows a structure similar to that of Pb-MOF, containing C-C (284.8 eV), C-O (286.1 eV), and O-C=O (288.4 eV) species. The O 1s spectrum contains C=O (531.4 eV) and C-OH (532.5 eV) peaks. An additional peak was observed at 533.7 eV, which can be attributed to adsorbed water molecules or free hydroxyl groups (-OH). The binding energies of Pb 4f Pb $4f_{7/2}$ and Pb $4f_{5/2}$ are located at 139.0 eV and 143.9 eV, respectively, which are in agreement with the values of Pb-MOF, suggesting a similar valence and chemical environment for Pb.

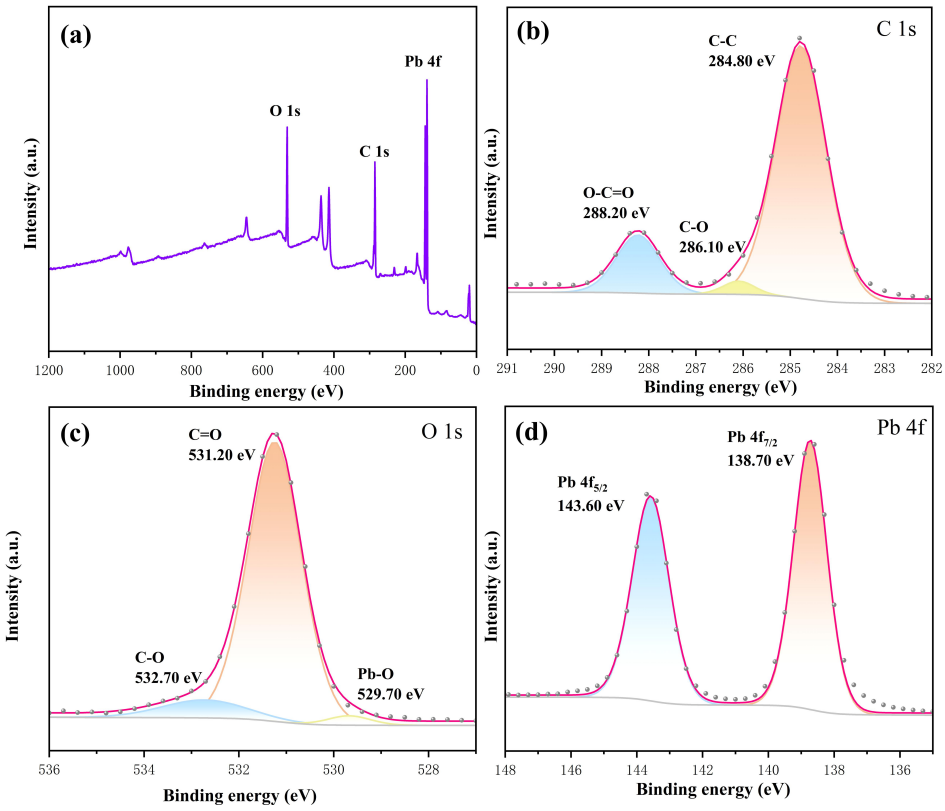

Fig. S2 XPS map of Pb-MOF-2, (a) full spectrum; (b) C 1s; (c) O 1s; (d) Pb 4f

As shown in Fig. S2, the C 1s spectrum shows the standard carbon species peaks; C-C (284.8 eV), C-O (286.1 eV) and O-C=O (288.2 eV). C=O (531.2 eV), C-O (532.7 eV) and Pb-O (529.7 eV) species are present in the O 1s spectrum. The binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ in Pb 4f are located at 138.7 eV and 143.6 eV, respectively.The binding energies are negatively shifted by about 0.3 eV compared to Pb-MOF.

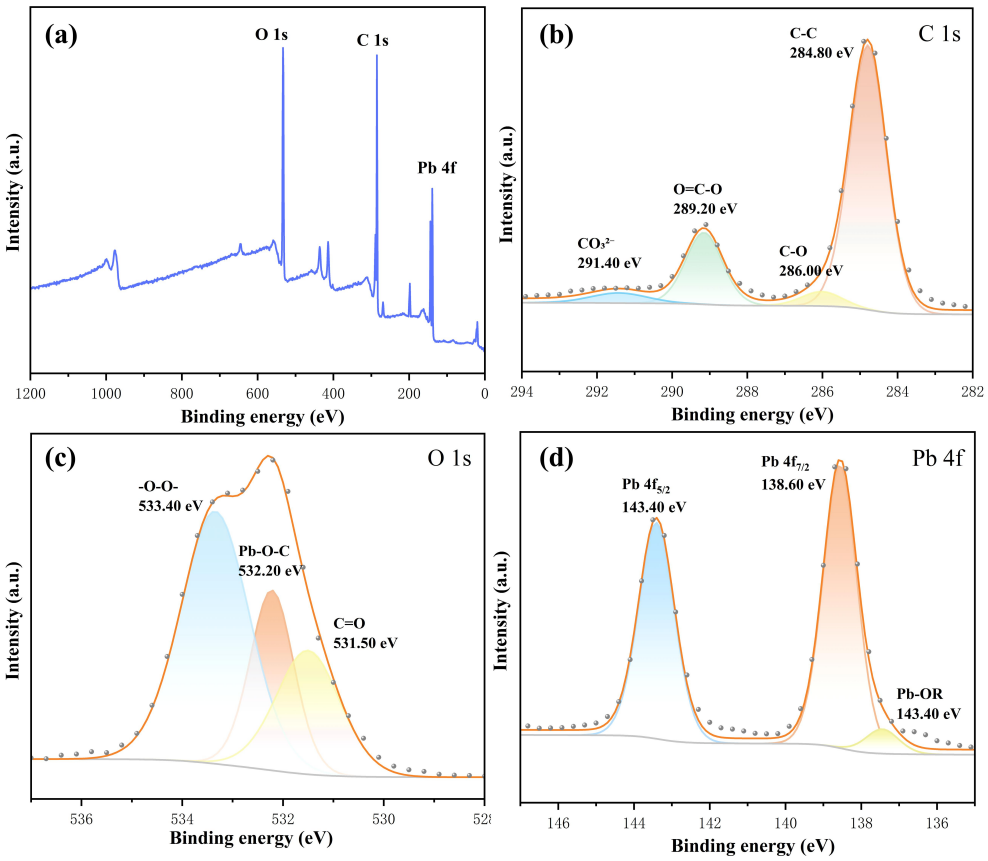

Fig. S3 XPS map of Pb-MOF-3, (a) full spectrum; (b) C 1s; (c) O 1s; (d) Pb 4f

As shown in Figure S3, in addition to the C-C (284.8 eV), C-O (286.0 eV), and O-C=O (289.2 eV) peaks in the C 1s, there is a strongly characterised peak at 291.4 eV, which is usually attributed to the carbonate CO_3^{2-} species.The O 1s spectrum is more complex and three peaks are proposed to be synthesised: C=O (531.5 eV), Pb-O-C (532.2 eV) and a peak at 533.4 eV, which may be related to peroxy groups (-O-O-) or strongly adsorbed water. The main double peaks of Pb 4f are located at 138.6 eV (Pb $4f_{7/2}$) and 143.4 eV (Pb $4f_{5/2}$), which are shifted negatively by about 0.4 eV compared to the Pb-MOF binding energy. the shape of the spectrum suggests that another Pb species (e.g., Pb-OR) may be present.

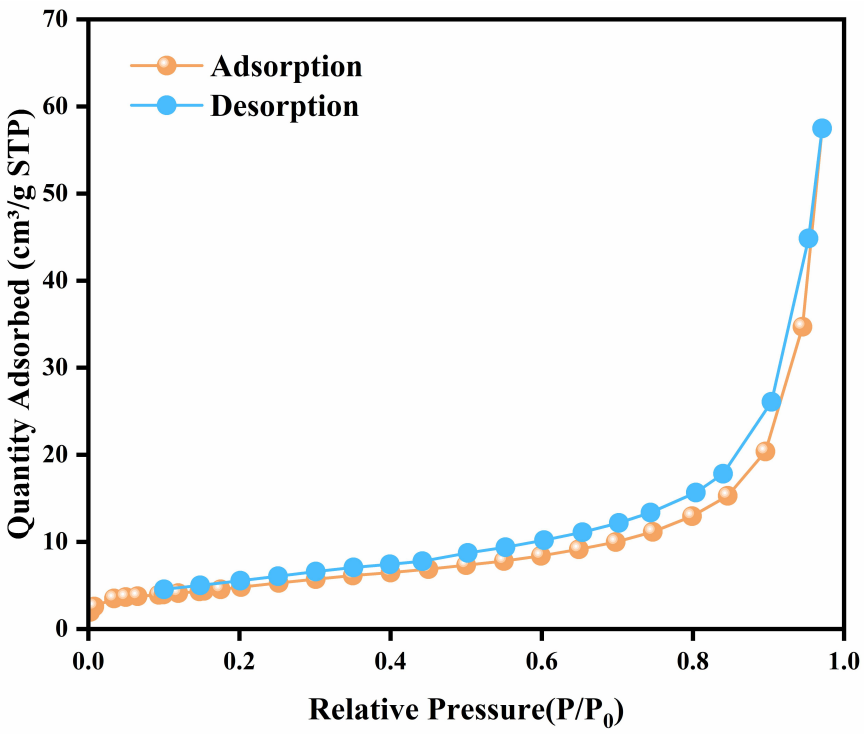

Fig. S4 N_2 adsorption-desorption isotherm of Pb-MOF measured at 77 K.

The measurement was performed at 77 K. The sample was degassed under vacuum at 120 °C for 6 h prior to the measurement. The BET surface area, calculated from the adsorption branch data, is 15.2 m^2/g. This relatively low value indicates a low-porosity material, which is consistent with the dense structure observed in the single-crystal X-ray diffraction analysis.

Table S1. Crystallographic parameters of compound Pb-MOF

Compound	**{[$Cu^{II}Fe^{III}_3O(tza)_6(H_2O)_3$]·$(NO_3)_2$·OH}$_n$**
Empirical formula	$C_{11}H_{11.57}O_{5.28}PbN$
Formula weight	449.49
Temperature(K)	153.15
Crystal system	monoclinic
Space group	$P2_1/n$
a(Å)	11.635(2)
b(Å)	6.5838(13)
c(Å)	17.079(3)
α(°)	90
β(°)	91.82(3)
γ(°)	90
Z	4
ρ_{calc}（g/cm^3）	2.283
μ（mm^{-1}）	12.916
F（000）	835.0
2θ range for data collection/°	6.632 to 54.974
h/k/l(max)	15, 8, 22
h/k/l	-11≤h≤16, -8≤k≤8, -21≤l≤22
Reflections collected	10103
Independent reflections	2971 [R_{int} = 0.0507, R_{sigma} = 0.0425]
Data/restraints/parameters	2971/198/173
Goodness-of-fit on F^2	1.122
Final R indices [I>2σ (I)]	R_1=0.0357, wR_2= 0.0723
R indices (all data)	R_1=0.0386, wR_2= 0.0738
Largest difference peak and hole(e. A^{-3})	1.33/-1.62
*volume(*A^3*)*	1307.6(4)

Table S2. Geometric parameters of compound Pb-MOF bond length (Å)

bond length (Å)			
Pb1-O1	2.494(4)	N1-C10	1.464(12)
Pb1-O2[1]	2.545(4)	N1-C11	1.444(12)
Pb1-O3	2.479(4)	C1-C2	1.366(8)
Pb1-O4	2.520(4)	C1-C3[3]	1.398(8)
Pb1-O6	2.619(5)	C2-C3	1.384(8)
Pb1-C8	2.861(6)	C2-C4	1.515(8)
O1-C4	1.270(7)	C3-C1[3]	1.398(8)
O2-Pb1[2]	2.545(4)	C5-C6	1.376(9)
O2-C4	1.266(7)	C5-C7[4]	1.408(8)
O3-C8	1.270(8)	C6-C7	1.396(9)
O4-C8	1.263(7)	C7-C5[4]	1.408(8)
O6-C9	1.246(10)	C7-C8	1.485(8)
N1-C9	1.331(10)		

13/2-X,1/2+Y,3/2-Z; 23/2-X,-1/2+Y,3/2-Z; 32-X,1-Y,2-Z; 41-X,2-Y,2-Z

Table S3. Compound Pb-MOF geometric parameters Bond angle (º)

Bond angle (º)			
O1-Pb1-O21	87.44(14)	C11-N1-C10	118.7(8)
O1-Pb1-O4	69.61(14)	C2-C1-C3[3]	120.3(6)
O1-Pb1-O6	148.15(17)	C1-C2-C3	119.9(5)
O1-Pb1-C8	70.95(16)	C1-C2-C4	120.2(5)
O21-Pb1-O6	83.19(16)	C3-C2-C4	120.0(5)
O21-Pb1-C8	100.23(16)	C2-C3-C1[3]	119.8(6)
O3-Pb1-O1	78.66(16)	O1-C4-C2	117.7(5)
O3-Pb1-O21	126.30(14)	O2-C4-O1	122.7(5)
O3-Pb1-O4	52.41(14)	O2-C4-C2	119.5(5)
O3-Pb1-O6	82.59(17)	C6-C5-C7[4]	120.8(6)
O3-Pb1-C8	26.29(16)	C5-C6-C7	119.9(6)
O4-Pb1-O21	74.05(13)	C5[4]-C7-C8	120.4(5)
O4-Pb1-O6	78.54(17)	C6-C7-C5[4]	119.3(5)
O4-Pb1-C8	26.19(15)	C6-C7-C8	120.3(5)
O6-Pb1-C8	80.85(18)	O3-C8-Pb1	59.9(3)
C4-O1-Pb1	101.7(4)	O3-C8-C7	119.2(5)
C4-O2-Pb12	128.3(4)	O4-C8-Pb1	61.7(3)
C8-O3-Pb1	93.9(4)	O4-C8-O3	121.3(5)
C8-O4-Pb1	92.1(3)	O4-C8-C7	119.5(5)
C9-O6-Pb1	123.7(5)	C7-C8-Pb[1]	175.2(4)
C9-N1-C10	120.4(8)	O6-C9-N1	123.8(8)
C9-N1-C11	120.7(8)		

13/2-X,1/2+Y,3/2-Z; 23/2-X,-1/2+Y,3/2-Z; 32-X,1-Y,2-Z; 41-X,2-Y,2-Z

Table S4. The average crystallite sizes of the four samples estimated from the Scherrer equation

Sample	crystallite size(nm)
Pb-MOF	68.20
Pb-MOF-1	24.41
Pb-MOF-2	7.49
Pb-MOF-3	48.70