Supporting Information

In situ synthesis of oxidized MXene-based metal cobalt spinel nanocomposites for an excellent promotion in thermal decomposition of ammonium perchlorate

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Reagents and chemicals

Titanium (Ti, 300 mesh) and Aluminum (Al, 300 mesh) powders were purchased from Yunfu Nanotech Co. Ltd. (Shanghai, China). Metal carbides (TiC) were 6~10 μm in particle size and were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Lithium fluoride (LiF) at analytical grade was also bought from Aladdin Industrial Co. Ltd. (Shanghai, China). All chemicals were used as initial state without any purification.

Synthesis of MAX phase (Ti_3AlC_2) and MXene ($Ti_3C_2T_x$)

The Ti_3AlC_2 (MAX) powders were synthesized by a hot-pressed sintering technique. The initial powders of Ti, Al and TiC with a molar ratio of Ti : Al : C = 3.0 : 1.2 : 1.8 were ball-milled for 10 h. The mixture was heated to 1350 °C for 30 min in Argon atmosphere under a pressure of 25.0 MPa. After cooling to room temperature, the sample was crushed in a mortar and pestle, and then sieved through a sieve (400 meshes) to obtain MAX powders less than 44.0 μm in diameter. MAX powder (2.0 g) was immersed in 20.0 mL LiF-HCl solution (> 40 wt%) by stirring for 24 h at 60.0 °C to completely remove the Al layers. Then the solution was centrifuged and rinsed several times using deionized water to remove HF until the pH of the solution attained 5.0-6.0. The obtained MXene powder was washed and dried in vacuum at 40.0 °C for 24 h.

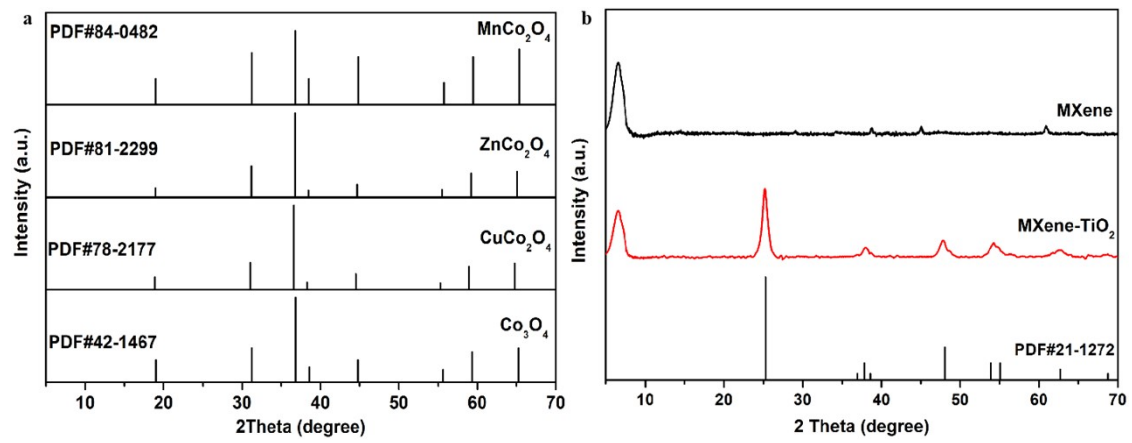Figure S1. (a) XRD standard cards of MnCo$_2$O$_4$, ZnCo$_2$O$_4$, CuCo$_2$O$_4$ and Co$_3$O$_4$. (b) XRD spectra of bare MXene and MXene-TiO$_2$ and XRD standard cards of TiO$_2$.
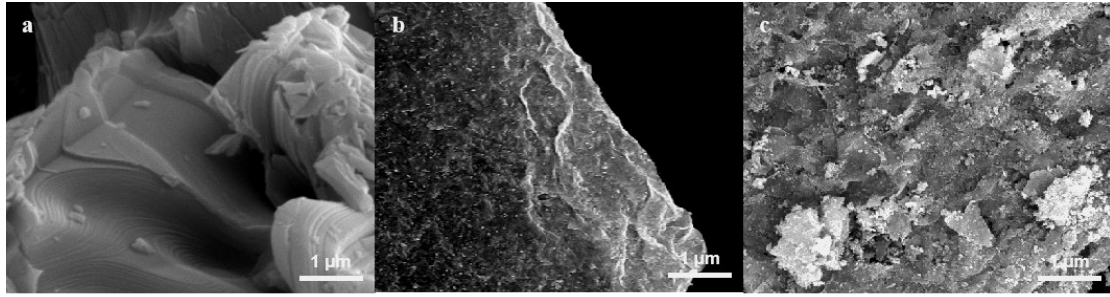
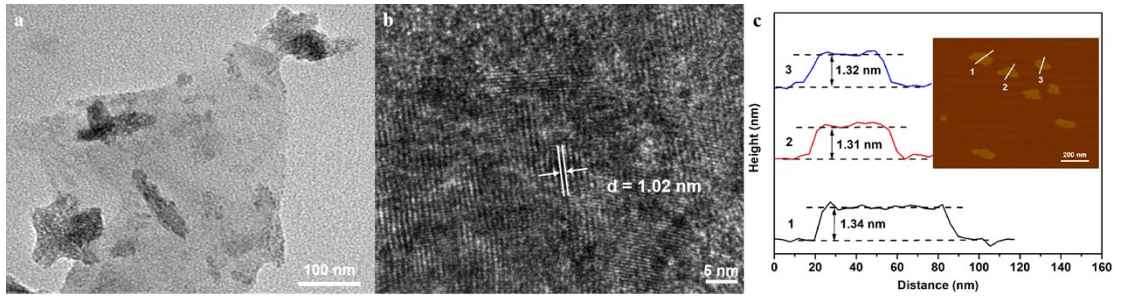Figure S2. SEM images of (a) MAX, (b) MXene and (c) MC.

Figure S3. (a) TEM and (b) HTEM images of MXene. (c) AFM-measured thickness of MXene. Inset: AFM image of MXene.
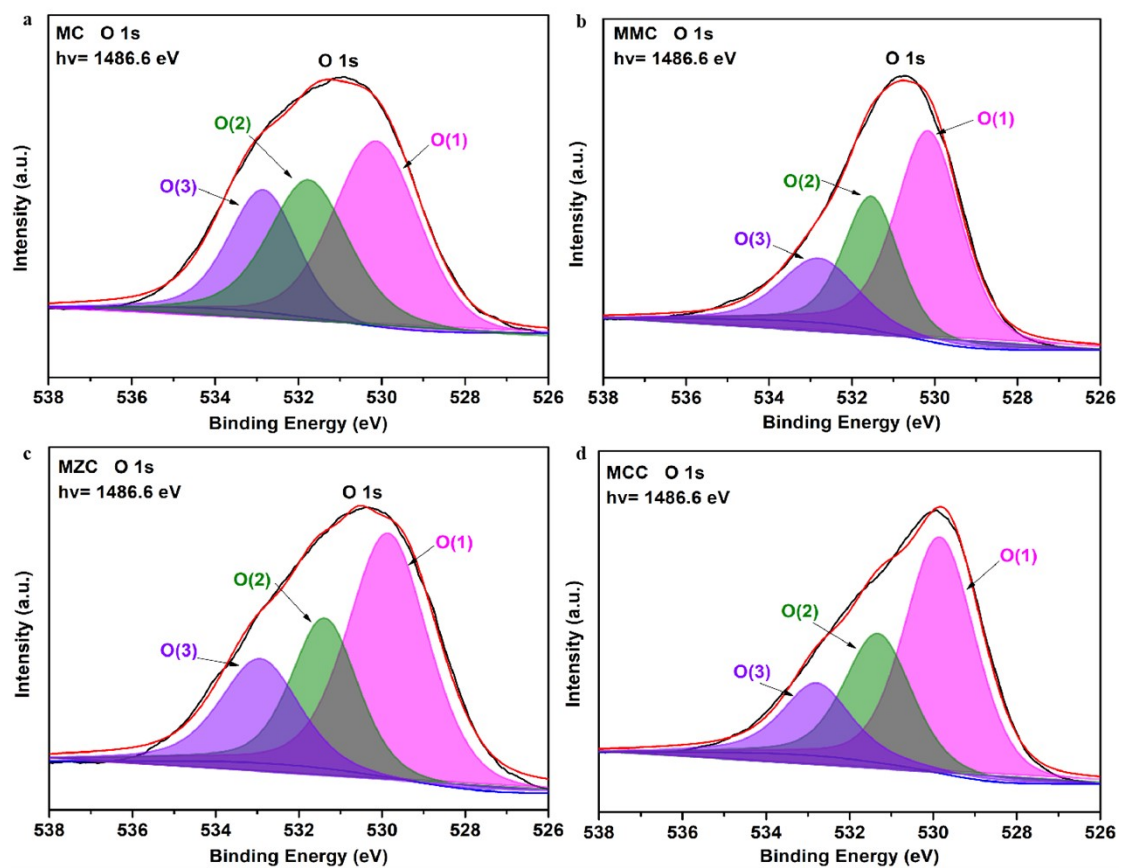
Figure S4. High resolution XPS spectra of O 1s for (a) MC, (b) MMC, (c) MZC and (d) MCC.
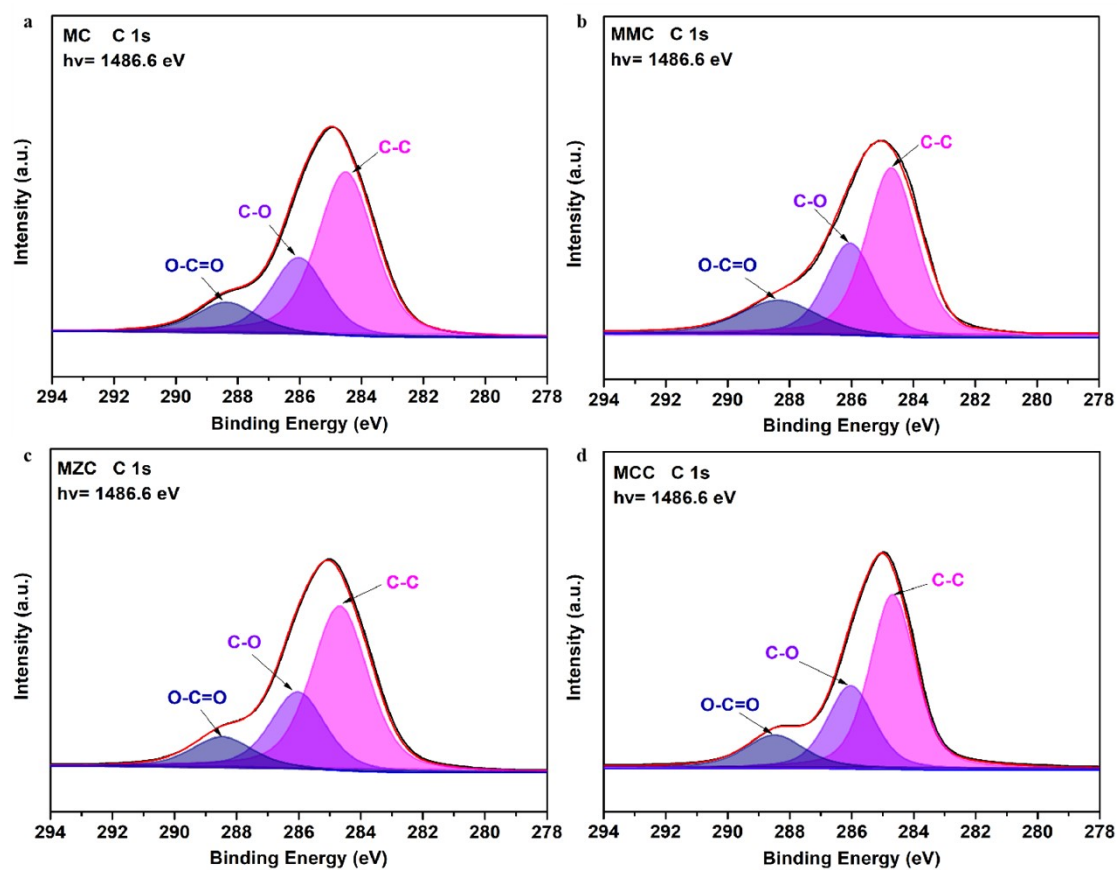
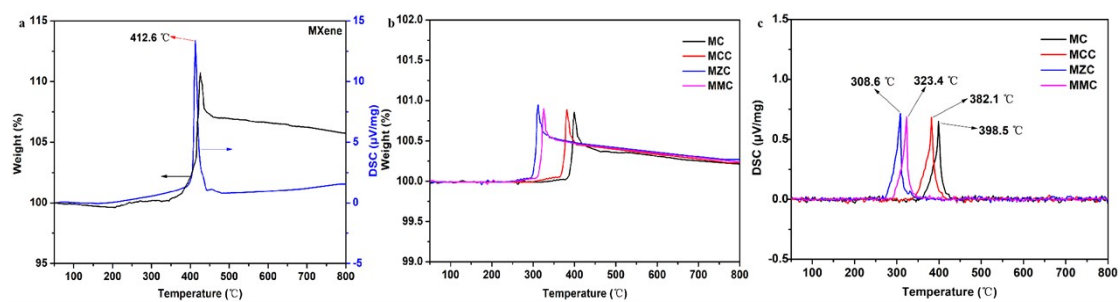Figure S5. High resolution XPS spectra of C 1s for (a) MC, (b) MMC, (c) MZC and (d) MCC.

Figure S6. (a) TGA-DSC curves of bare MXene from room temperature to 800 °C in air atmosphere. (b) TGA and (c) DSC curves of MC, MCC, MZC and MMC from room temperature to 800 °C in air atmosphere.

Kissinger correlation and Arrhenius equation

Activation energy is an important indicator to reflect the pyrolysis behavior of AP. In the present work, Kissinger method is widely used to determine the apparent activation energy (E_a) and the pre-exponential factor (A). The relation between decomposition temperature and heating rate using Kissinger equation is defined as Equation S(1) and the equation of *lnA* can be described as Equation S(2).

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_P} \tag{S1}$$

$$\ln A = \ln\left(\frac{\beta}{T_P^2}\right) + \left(\frac{E_a}{RT_P}\right) - \ln\left(\frac{R}{E_a}\right) \tag{S2}$$

where β is the heating rate (°C·min⁻¹), T_p is the HTD temperature (K), R represents the ideal gas constant (8.314 J·mol⁻¹·K⁻¹), E_a is the activation energy (kJ·mol⁻¹), and A represents the pre-exponential factor. The Kissinger method was employed for the kinetic analysis, which is based on the plot of $\ln(\beta/T_p^2)$ varying linearly with $1/T_p$. Reciprocal of the DSC peak temperature in absolute ($1/T_p$). The slope of the straight line plot is used for the calculation of E_a.

Based on Arrhenius equation and the kinetic parameters calculated from Kissinger equation, the reaction rate constant (k) can be obtained. The Arrhenius equation is described as follows.

$$k = A\exp\left(\frac{-E_a}{RT_P}\right) \tag{S3}$$

where T_p is the HTD temperature (K), R represents the ideal gas constant (8.314 J·mol⁻¹·K⁻¹), E_a is the activation energy (kJ·mol⁻¹), A represents the pre-exponential factor, and k is the reaction rate constant.
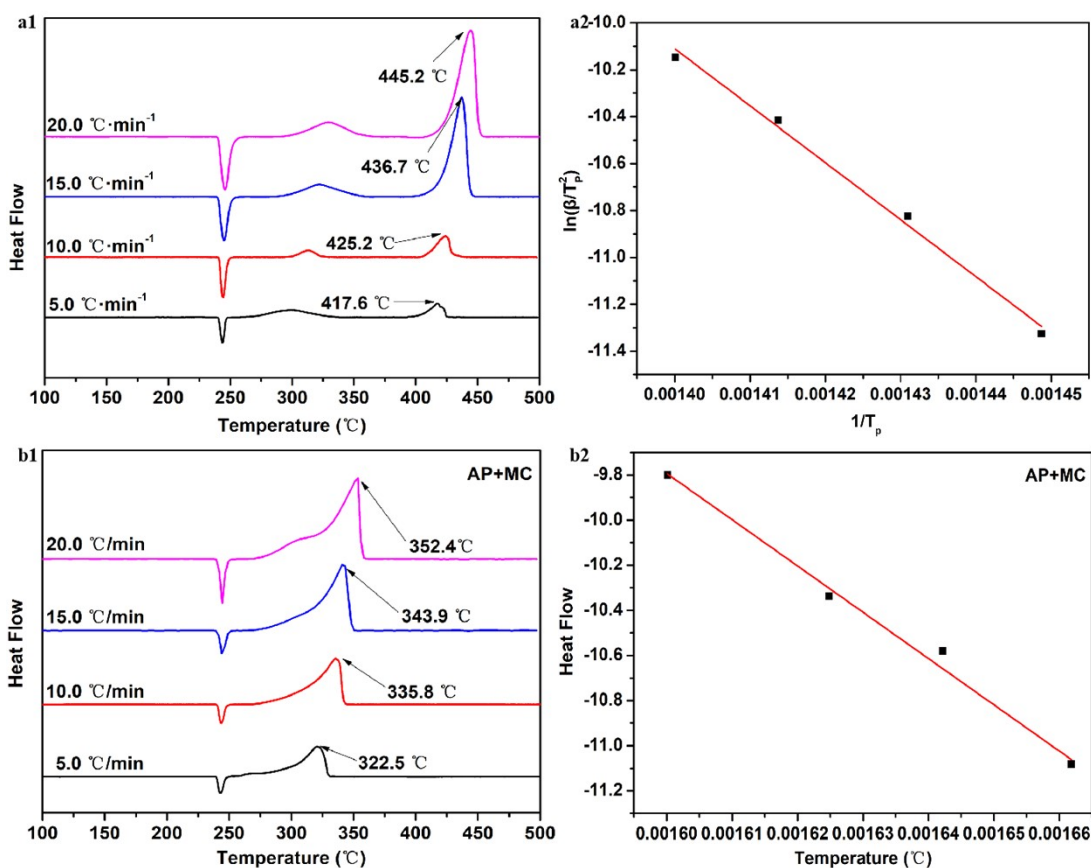
Figure S7. (a1) DSC curves of pure ammonium perchlorate (AP) at different heating rate (5.0, 10.0, 15.0 and 20.0 °C·min^{-1}), (a2) dependence of $\ln(\beta/T_p^2)$ on $1/T_p$ for pure AP, (b1) DSC curves of AP in the presence of 2.0 wt% MC at different heating rate (5.0, 10.0, 15.0 and 20.0 °C·min^{-1}) and (b2) dependence of $\ln(\beta/T_p^2)$ on $1/T_p$ for AP in the presence of 2.0 wt% MC.

Table S1 The parameters calculated for the thermal decomposition of pure AP and AP in presence of 2 wt% catalysts (MMC, MZC, MCC, MC).

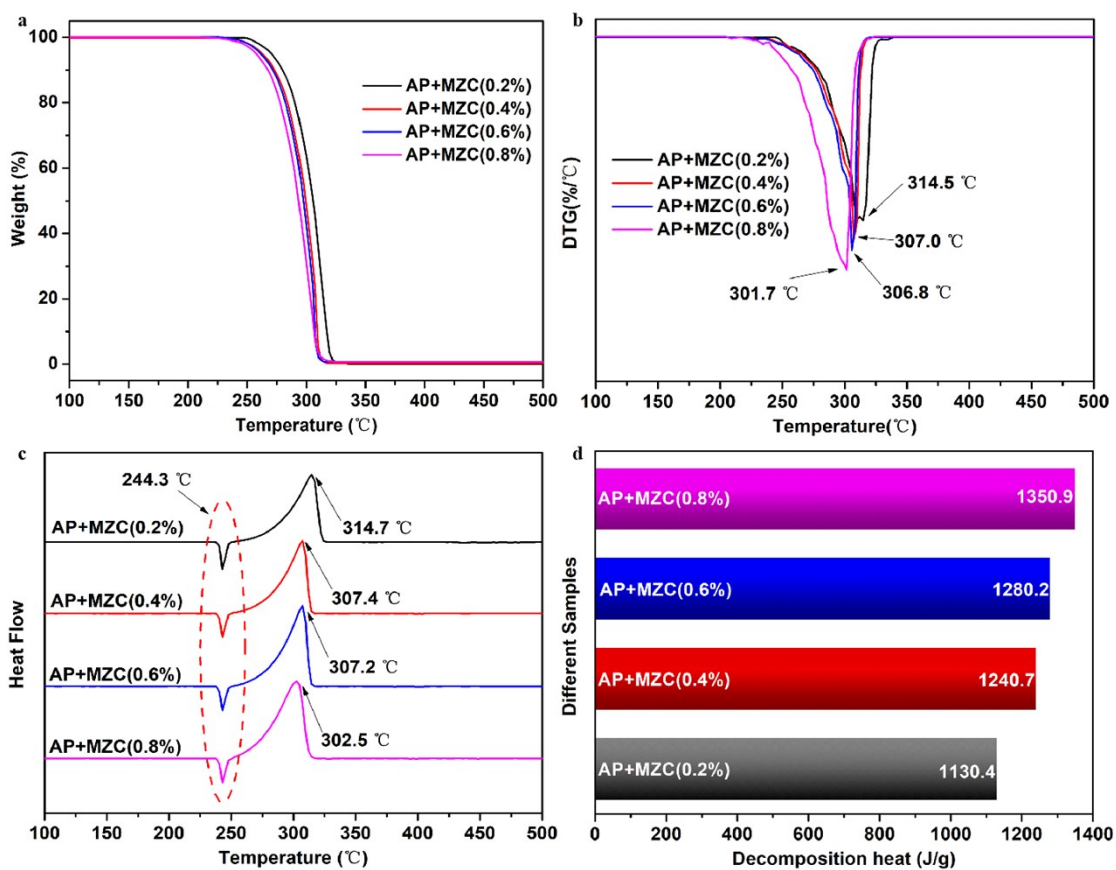| Sample	E_a (kJ·mol^{-1})	lnA	k (s^{-1})×10^{-3}
Pure AP	209.6	28.0	0.31
AP+MMC	142.4	22.5	0.56
AP+MZC	104.5	15.2	1.65
AP+MCC	160.3	24.2	0.42
AP+MC	172.4	26.1	0.35

Figure S8. (a) TGA, (b) DTG and (c) DSC curves of AP in the absence and presence of different ratios of MZC (0.2%, 0.4%, 0.6%, 8.0%). (d) Heat release during the decomposition of AP with catalysts.

Table S2. HTD temperature of AP in the absence and presence of different mass ratios of MZC from DSC curves, and heat release during the decomposition of AP with different mass ratios of MZC.

Sample	HTD temperature (°C)	Reduced temperature (°C)	Decomposition heat (J·g^{-1})
AP	425.2	-	295.2
AP+MZC(0.2%)	314.7	110.5	1130.4
AP+MZC(0.4%)	307.4	117.8	1240.7
AP+MZC(0.6%)	307.2	118	1280.2
AP+MZC(0.8%)	302.5	122.7	1350.9
AP+MZC(1.0%)	300.7	124.5	1367.4
AP+MZC(2.0%)	297.1	128.1	1409.6
AP+MZC(4.0%)	282.9	142.3	1476.5
AP+MZC(6.0%)	276.0	149.2	1526.8
AP+MZC(8.0%)	281.6	143.6	1450.2