

**Graphene oxide functionalized energetic coordination polymer  
possesses good thermostability, heat release and combustion catalytic  
performance for ammonium perchlorate**

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## 1 Preparation

### 1.1 Preparation of GO

Typically, GO was prepared using natural graphite powder by a modified Hummers method. Natural graphite powder (3.0 g) was oxidized by reacting with 70 mL concentrated sulfuric acid at room temperature. Furthermore, the sodium nitrate (1.5 g) was added into the reaction vessel. After that, the reaction mixture was immersed in an ice bath. The potassium permanganate (9.0 g) was slowly added under vigorous agitation. Notably, the temperature of the suspension was below 20 °C. Subsequently, the ice bath was removed and replaced by a water bath and the temperature of reaction system was kept at 30-40 °C about 30 min, producing a thick paste. 140mL water was added. The reaction solution was gradually heated to 95 °C and stirred for 15 min. 500 mL water was added and followed by addition of 20 mL H<sub>2</sub>O<sub>2</sub> (30%), leading the color of reaction mixture changing from brown to yellow. When the reaction was accomplished, the mixture was filtered and washed with 250 mL HCl aqueous solution in order to remove metal ions. Successively, the mixture was washed with water and centrifugated to remove the acid. The resulting solid was dispersed in water by ultrasonication for 1 h to make a GO aqueous dispersion (0.68 wt%). The obtained dispersion was centrifuged at 4000 rpm to remove assemblies. The crude product was purified by dialysis for 2 weeks to remove the salt impurities.

### 2.1 Preparation of **GO-Cu(II)-AmTZ/AP**

#### 2.1.1 **GO-Cu(II)-AmTZ/AP (1:1)**

40 mg of AP was dissolved in 20 mL of acetone first. Then, 40 mg of **GO-Cu(II)-AmTZ** was added to the mixture, stirring the mixture for 3 h. The **GO-Cu(II)-AmTZ/AP (1:3)** composites were prepared after freeze drying.

#### 2.1.2 **GO-Cu(II)-AmTZ/AP (1:2)**

80 mg of AP was dissolved in 20 mL of acetone first. Then, 40 mg of **GO-Cu(II)-AmTZ** was added to the mixture, stirring the mixture for 3 h. The **GO-Cu(II)-AmTZ/AP (1:3)** composites were prepared after freeze drying.

#### 2.1.3 **GO-Cu(II)-AmTZ/AP (1:3)**

160 mg of AP was dissolved in 20 mL of acetone first. Then, 40 mg of **GO-Cu(II)-AmTZ** was added to the mixture, stirring the mixture for 3 h. The **GO-Cu(II)-AmTZ/AP** (1:3) composites were prepared after freeze drying.

## 2. Kissinger's and Ozawa-Doyle's methods

Herein, the kinetics parameters of the exothermic process of **1** were studied by using Kissinger's and Ozawa-Doyle's methods.<sup>1-3</sup> The Kissinger (1) and Ozawa (2) equations are as follows, respectively:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E} - \frac{E}{R} \frac{1}{T_p} \quad (1)$$

$$\log\beta + \frac{0.4567E}{RT_p} = C \quad (2)$$

Where  $E$  is the apparent activation energy;  $A$  is the pre-exponential factor;  $T_p$  is the peak temperature;  $R$  is the gas constant;  $\beta$  is the linear heating rate and  $C$  is constant. The exothermic peak temperatures of **GO-Cu (II)-AmTZ** were determined on the basis of four different heating rates of 5, 10, 15, 20 °C min<sup>-1</sup> (Figure 3). It imports collected data into the formula (1) and (2), which can be used to estimate the values of reaction apparent activation energy  $E_k$  and  $E_o$ , pre-exponential factor  $A_k$  and linear correlation coefficients  $R_k$  and  $R_o$  (subscript k stand for Kissinger's method, o stand for Ozawa's method). The experimental and calculated results are shown in Table S1. The computational results using different methods are similar and within the normal scope of kinetics parameters of such thermal decomposition reaction. The relevant Arrhenius equation of **GO-Cu (II)-AmTZ** can be described by employing the obtained  $E_a$  (the average of  $E_k$  and  $E_o$ ) and  $\ln A$  values, as follow:  $\ln k = 10.38 - 290.04 \times 10^3 / RT$ . The equation can be used to estimate the rate constant of the thermal decomposition process of **GO-Cu (II)-AmTZ** and predict its thermal decomposition mechanism.

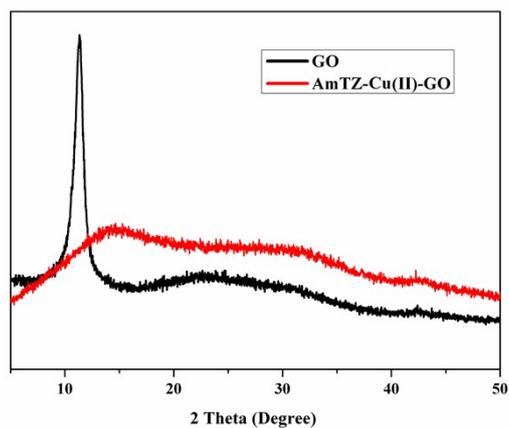


Figure S1 The X-ray diffraction (XRD) patterns of GO and **GO-Cu (II)-AmTZ**.

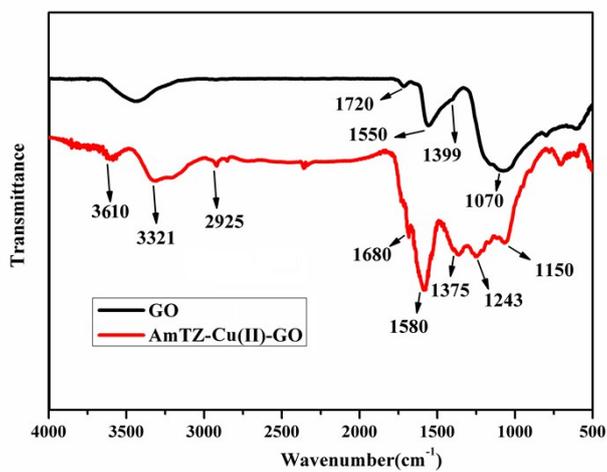


Figure S2 The Fourier transform-infrared spectroscopy (FTIR) of GO and **GO-Cu (II)-AmTZ**.

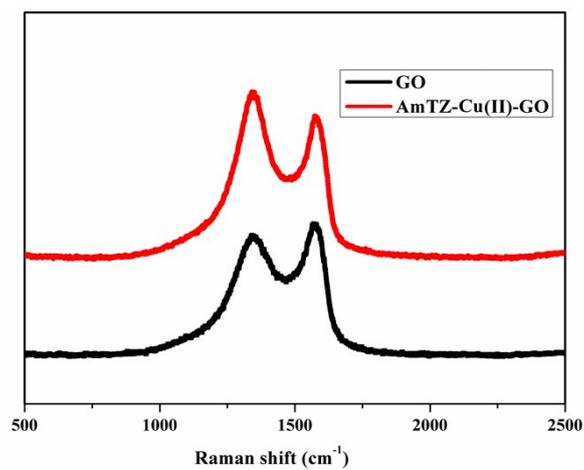


Figure S3 Raman spectra of bare GO and **GO-Cu (II)-AmTZ**.

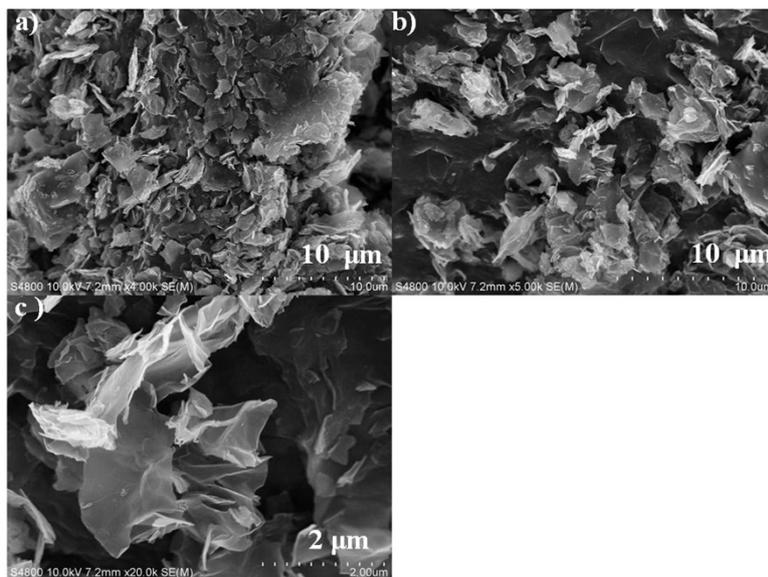


Figure S4 SEM image of **GO-Cu (II)-AmTZ/AP** composites.

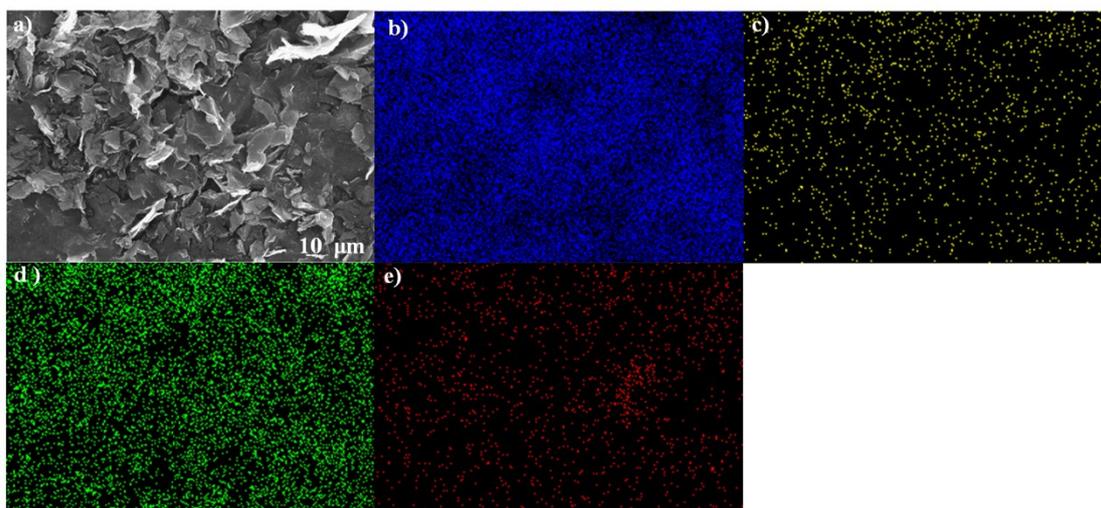


Figure S5 The SEM of selected area for EDS mapping in **GO-Cu (II)-AmTZ/AP** (a); EDS elemental distribution mapping of C, N, O, Cl (b, c, d, e) in **GO-Cu (II)-AmTZ/AP**.

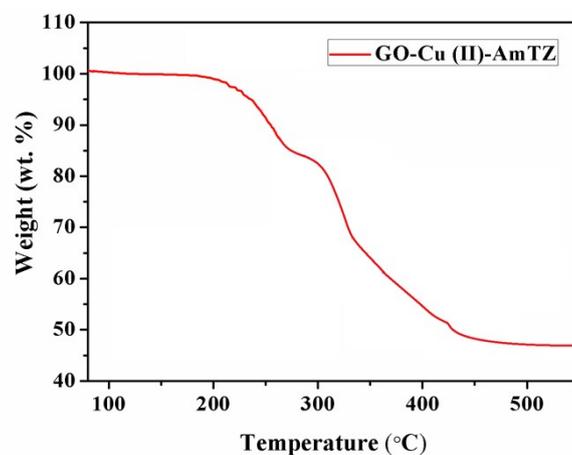


Figure S6 The TGA profile of **GO-Cu (II)-AmTZ** was carried out under a flow of

dry oxygen-free nitrogen as the atmosphere with a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ .

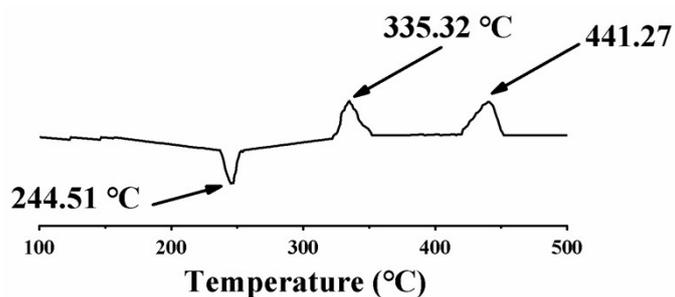


Figure S7 DSC measurement with the heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  for AP.

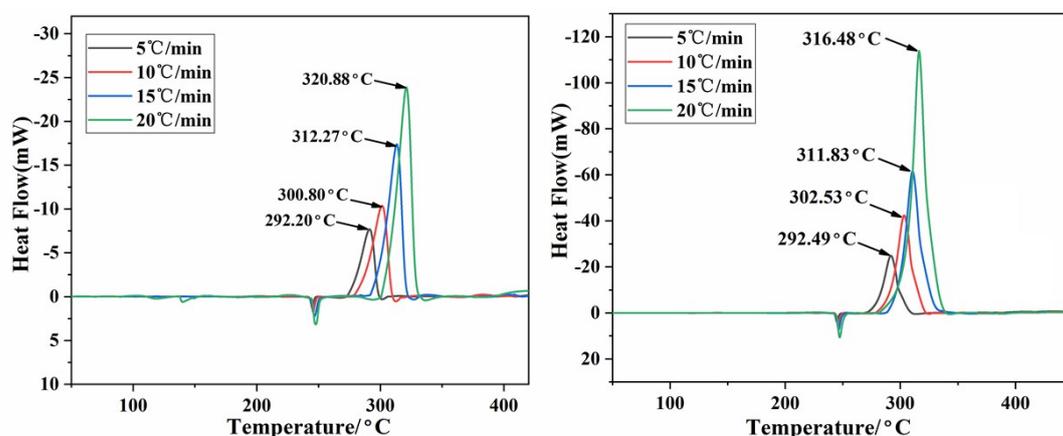


Figure S8 DSC measurements with four different heating rates of 5, 10, 15 and  $20^{\circ}\text{C}\cdot\text{min}^{-1}$  for **GO-Cu (II)-AmTZ/AP** (a, 1:1; b, 1:2), respectively.

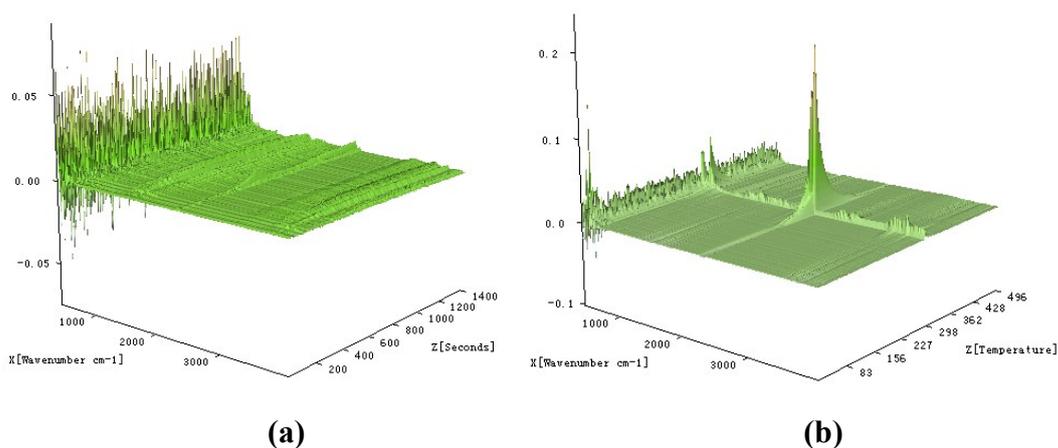


Figure S9 Thermogravimetry coupled with infrared spectrometry (TG/IR) were employed to evaluate the decomposition mechanisms of **GO-Cu (II)-AmTZ** (a) and **GO-Cu (II)-AmTZ/AP** (b) under a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ .

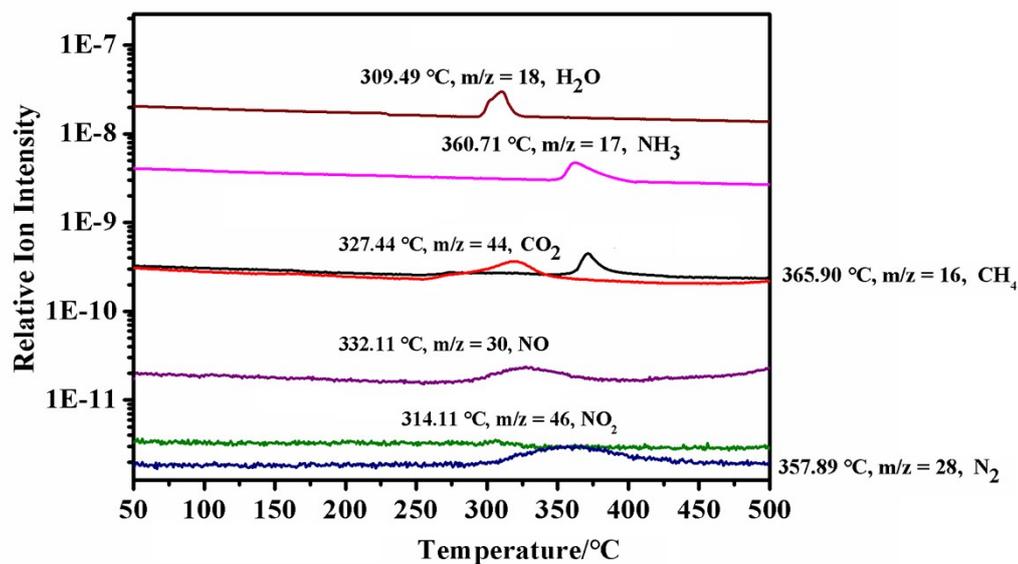


Figure S10 Temperature dependency of the ion flows from non-isothermal decomposition for **GO-Cu (II)-AmTZ** under a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  using thermogravimetry coupled with mass spectrometry (TG/MS) technique.

### 3. Notes and references

- 1 H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702–1706.
- 2 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1881–1886.
- 3 C. Doyle, *J. Appl. Polym. Sci.*, 1961, **5**, 285–292.