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## PAPER

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## 1. Introduction

Ammonium perchlorate (AP) is the most common energetic oxidant in composite solid propellants (CSPs). The thermal decomposition characteristics of AP directly influence the burning behavior of CSPs.<sup>1,2</sup> Extensive studies reveal the catalytic activity of transition metals oxides which can signicantly improve the performance of the decomposition of AP.<sup>3–9</sup> Among the numerous varieties of transition metals oxides, spinel oxides (nanoferrites) due to their size, surface site and abundance of cations, for co-ordination sites, can increase activity of chemical reactivity<sup>10</sup> and are widely applied in the fields of electronics, catalysis, adsorbents, etc. Previous studies have suggested that the increase of specific surface area of a catalyst would dramatically enhance its catalytic performance on thermal decomposition of AP.11,12 However, nanoparticles (NPs) are likely to aggregate due to their large surface energy, which will lead to the decrease of specific surface area and further influence their catalytic performance in the decomposition process.

Enormous attention has been attracted on graphene due to its excellent special surface properties, high conductivity and thermal stability.13,14 It has been proved that the twodimensional structure of graphene sheets allows them to be the perfect dispersing-substrate for the NPs and acts as efficient

## Facile preparation of rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids and its catalytic performance during the thermal decomposition of ammonium perchlorate

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Reduced graphene oxide/metal ferrite (rGO/MFe<sub>2</sub>O<sub>4</sub>, M = Cu, Co, Ni) nanohybrids are successfully prepared through a simple, one-step hydrothermal method. The  $rGOMFe<sub>2</sub>O<sub>4</sub>$  nanohybrids are characterized by XRD, TEM, FT-IR, XPS, Raman and BET surface area measurements. The  $rGOMFe<sub>2</sub>O<sub>4</sub>$ nanohybrids demonstrate amazing catalytic activities on the thermal decomposition of ammonium perchlorate (AP). DSC results indicate that  $rGO/MFe_2O_4$  nanohybrids (3 wt%), could decrease the decomposition temperature of pure AP from 424.7  $^{\circ}$ C to 329.1  $^{\circ}$ C, 338.3  $^{\circ}$ C, and 364.8  $^{\circ}$ C, respectively. This enhanced catalytic performance is mainly attributed to the synergistic effect of NPs and rGO. The activation energy  $(E_a)$  of AP mixed with nanohybrids is investigated by two isoconversion methods, Flynne–Walle–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS), on a conversion degree  $(\alpha)$  range from 0.05 to 0.95. The values of  $E_a$  calculated from the above two methods matched with each other. A strong dependence of  $E_a$  on  $\alpha$  is observed, indicating a complex decomposition process. **PAPER**<br> **EXERCTION THE SET AND STATE CONFIDENCE CONTRESS CONFIDENTIAL CONTRESS CONTRE** 

solid conductive supporters for enabling good contact between nanoferrites.<sup>15</sup>

Herein, we prepared rGO/MFe<sub>2</sub>O<sub>4</sub> ( $M = Cu$ , Co, Ni) nanohybrids in a facile one-pot way. We demonstrated a comparative study about the catalytic activities of nanohybrids on thermal decomposition of AP. As far as we know, no study involving rGO/  $MFe<sub>2</sub>O<sub>4</sub>$  nanohybrids as a series of catalysts for the decomposition of AP has been reported.



Fig. 1 XRD patterns of (a) rGO/CuF, (b) rGO/CoF, (c) rGO/NiF nanohybrids.

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Fig. 2 TEM images of (a) rGO/CuF, (b) rGO/CoF, (c) rGO/NiF nanohybrids and (g) GO; HRTEM images of (d) rGO/CuF, (e) rGO/CoF, (f) rGO/NiF nanohybrids.

## 2. Experimental

### 2.1 Materials

Natural graphite powder was from Qingdao Graphite Factory. Potassium permanganate, sodium nitrate, concentrated

sulfuric acid, hydrogen peroxide (30%), hydrochloric acid, sodium hydroxide anhydrous, ethanol, nitrates of Cu, Co, Ni and Fe were obtained from Beijing Chemical Reagent Co. Ltd. All reagents used are analytical grade.

#### 2.2 Synthesis of rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids

GO was obtained from graphite powder in a modified Hummers way.<sup>16</sup> GO (72 mg) was added into deionized water (30 mL) with sonication.  $M(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (M = Cu, Co, Ni) (1 mmol)$  and  $Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O$  (2 mmol) was mixed into GO solution. The mixtures were added with NaOH solution until a pH value of 11– 12 reached under magnetic stirring. The viscous precipitates were moved into a 100 mL Teflon lined stainless-steel autoclave, heated overnight at 180 °C. The precipitates were centrifuged, rinsed with DI water and ethanol. The products labeled as rGO/ CuF, rGO/CoF, rGO/NiF with rGO content of 25 wt%, were put in oven at 60  $^{\circ}$ C. For comparison, same process was repeated to prepare pure CuF, CoF, NiF NPs and graphene.

#### 2.3 Characterization

X-ray powder diffraction (XRD) patterns of the nanohybrids were obtained using a Bruker D8-Advanced diffractometer. Transmission electron microscopy (TEM) and high-resolution (HRTEM) was measured on a JEOL, JEM-2100. The function groups were investigated by Fourier transform infrared spectra (FT-IR; Perkin Elmer). Raman spectra were investigated by a Raman spectrometer (Horiba JY HR-800). X-ray photoelectron spectroscopy (XPS) was characterized by a PHI Quantera system. Nitrogen adsorption/desorption isotherms were characterized by an BELSORP-max (ANKERSMID), Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area.

The rGO/MFe<sub>2</sub>O<sub>4</sub> ( $M = Cu$ , Co, Ni) nanohybrids, rGO and pure MF NPs were fully mixed with AP in the mass ratio of 1 wt%, 3 wt% and 5 wt%, respectively. The thermal properties of the above mixtures were investigated using a differential thermal analyzer (TGA-DSC, METTLER, 1/1600HT) with nitrogen gas (flow rate 50 mL min $^{-1}$ ).

## 3. Results and discussion

### 3.1 Characterization

The XRD patterns of as-prepared rGO/CuF, rGO/CoF, rGO/NiF nanohybrids are displayed in Fig. 1. For CuFe<sub>2</sub>O<sub>4</sub> (Fig. 1a), the peaks are at  $2\theta = 18.2^{\circ}, 30.1^{\circ}, 35.5^{\circ}, 43.2^{\circ}, 53.6^{\circ}, 57.0^{\circ}, 62.6^{\circ}$ , 74.1°, which correspond to the crystal planes of  $(111)$ ,  $(220)$ , (311), (400), (422), (511), (440), (533), respectively. The positions of all diffraction peaks (Fig. 1a–c) can be well assigned to standard structure of CuFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> (JCPDS no. 77-0010, 22-1086 and 86-2267), respectively. The average crystallite size of rGO/CuF, rGO/CoF, rGO/NiF nanohybrids, calculated from the three most intense peaks of each patterns by Scherrer equation<sup>17</sup> are 15.3, 12.6, and 9.8 nm, respectively.

The morphology of the as-synthesised rGO/CuF, rGO/CoF, rGO/NiF nanohybrids and GO were characterized by TEM. As shown in Fig. 2a–c,  $MFe<sub>2</sub>O<sub>4</sub>$  (M = Cu, Co, Ni) NPs are uniformly dispersed on rGO sheets. There are no NPs fell off the rGO sheets after long time sonication of the samples, indicating the strong interaction between NPs and rGO sheets. Fig. 2g shows a wrinkled waves-like textures of GO sheets. The HRTEM images of CuF, CoF, NiF NPs, presented in Fig. 2d–f, display a clear crystal lattice with a spacing of 0.25 nm, 0.31 nm, 0.31 nm,

respectively, corresponding to (311), (111), (111) plane of  $MFe<sub>2</sub>O<sub>4</sub>$  (M = Cu, Co, Ni) cubic structure.

Fig. 3 represents FTIR spectra of GO and rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni). For GO (Fig. 3a), the broad absorption at  $3411 \text{ cm}^{-1}$ is ascribed to O–H stretching mode. The other peaks are due to the stretching vibration of carboxylic C=O (1735  $cm^{-1}$ ), aromatic C-C (1617 cm<sup>-1</sup>), C-OH (1407 cm<sup>-1</sup>), C-O-C (1214 cm<sup>-1</sup>) and alkoxy (1049  $\text{cm}^{-1}$ ), respectively.<sup>18</sup> For rGO/MFe<sub>2</sub>O<sub>4</sub> (Fig. 3b-d), peak intensity of oxygen-containing groups decreased obviously or disappeared gradually indicating that GO has been successfully reduced to rGO.<sup>19</sup> The peak at 1574  $cm^{-1}$ , is due to the skeletal vibration of rGO sheets. A new absorption at around  $600 \text{ cm}^{-1}$  is assigned to the metal oxygen bonds.

Fig. 4 displays the XPS spectra of rGO/MFe<sub>2</sub>O<sub>4</sub> ( $M = Cu$ , Co, Ni) nanohybrids and GO. Fig. 4a is clearly indicated that the C/O ratios in the  $rGO/MFe<sub>2</sub>O<sub>4</sub>$  nanohybrids increase obviously compared with that of GO. In Fig. 4b, the peaks at around 723.0 and 710.6 eV corresponds to Fe2 $p_{1/2}$  and Fe2 $p_{3/2}$ , respectively.<sup>20</sup> In Fig. 4c–e, two peaks at 932.9 eV and 952.7 eV are assigned to Cu2p<sub>1/2</sub> and Cu2p<sub>3/2</sub>, respectively.<sup>21</sup> Two peaks at 779.2 eV and 880.8 eV is ascribed to the Co  $2p_{3/2}$  and Co $2p_{1/2}$ , respectively.<sup>22</sup> Two peaks at 855.0 and 872.7 eV corresponds to  $Ni2p_{3/2}$  and Ni2 $p_{1/2}$ , respectively.<sup>23</sup> In Fig. 4f, four peaks at 284.1, 286.3, 287.5, 288.7 eV assigned to aromatic C=C/C-C, C-OH, C=O, O=C-O bonds, respectively.<sup>24</sup> Fig. 4g-i show that peak intensities of the epoxide and hydroxyl functional groups are remarkably decreased, suggesting the successful reduction of GO. Paper<br>
2. Symbol of GOMFig.O<sub>p</sub> (M = Cu, Co, N) mandphilds. Top Compactions Colline is licensed to the modifications are proposed under a creative Commons are the modifications and the symbol on 2018. Dependent in a modif

Fig. 5 displays Raman spectra of GO and rGO/MF ( $M = Cu$ , Co, Ni) nanohybrids. As can be seen in Fig. 5a, two peaks at around 1356  $\text{cm}^{-1}$  and 1597  $\text{cm}^{-1}$  corresponding to D and G band, respectively. In Fig. 5b and c, small shifting was seen in D and G bands suggesting oxygen-containing functional groups of GO are remarkably removed. The calculated intensity ratios of D and G band  $(I_D/I_G)$  of rGO/CuF, rGO/CoF, rGO/NiF and GO are 1.07, 1.09, 1.04, 0.90, respectively. The higher  $I_{\rm D}/I_{\rm G}$  values of rGO/MF nanohybrids suggest that GO sheets are successfully reduced.<sup>25</sup>



Fig. 3 FT-IR absorption spectra of (a) GO, (b) rGO/CuF, (c) rGO/CoF, (d) rGO/NiF nanohybrids.



Fig. 4 XPS spectra of the rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids and GO (a) survey, (b) Fe 2p, (c) Cu 2p, (d) Co 2p, (e) Ni 2p, (f) C 1s, (g) C 1s, (h) C 1s, (i) C 1s.

 $N_2$  adsorption/desorption isotherms tests are done to calculate specific surface area of pure NPs and  $rGOMF(M = Cu,$ Co, Ni) nanohybrids. As shown in Table 1, the BET value of rGO/



Fig. 5 Raman spectra of (a) GO, (b) rGO/CuF, (c) rGO/CoF and (d) rGO/NiF nanohybrids.

MF ( $M = Cu$ ,  $Co$ ,  $Ni$ ) is much higher than that of pure NPs, indicating that rGO sheets improved the dispersion of the NPs, which may resulting its improved catalytic activity.

### 3.2 The catalytic effect of the rGO/MFe<sub>2</sub>O<sub>4</sub> ( $M = Cu, Co, Ni$ ) nanohybrids on the thermal decomposition of AP

To investigated the catalytic behaviors of the catalysts, TG-DSC curves were tested at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. Fig. 6a shows DSC curves of pure AP. It indicates a three-stage decomposition process. In the first stage, peak centered at 247.4 °C, is in







Fig. 6 DSC curves of (a) pure AP, AP mixed with (b) rGO/CuF, (c) rGO/CoF, and (d) rGO/NiF (1 wt%, 3 wt%, 5 wt%) nanohybrids.

agreement with crystallographic transition from the orthorhombic to cubic form. In the second stage, peaks at 300.8  $^{\circ}\textrm{C},$ shows low-temperature decomposition (LTD) and peaks at 424.7 °C shows high-temperature decomposition (HTD).

However, Fig. 6b–d show the endothermic peak has no shifts, indicating that  $rGO/MFe<sub>2</sub>O<sub>4</sub>$  nanohybrids have no impact on the endothermic process but obvious peak temperature decreasing is taken place in LTD and HTD process.

In Fig. 6b, LTD peak has no signicant changes. As shown in Fig. 6c and d, only one exothermic peak (HTD peak) is obvious for 5 wt%, compared with two exothermic peaks for 1 wt% and 3 wt%. The HTD peak temperature of  $AP/FGO/MFe<sub>2</sub>O<sub>4</sub>$  (M = Cu, Co, Ni) mixtures are reduced by 90.2  $^{\circ}$ C, 67.4  $^{\circ}$ C, 40.9  $^{\circ}$ C (1 wt%), 95.6  $^{\circ}$ C, 86.4 °C, 59.9 °C (3 wt%), 98.1 °C, 97.2 °C, 64.2 °C (5 wt%), respectively. Meanwhile, the released energy of the mixtures (3% wt) is 1523.5 J  $g^{-1}$ , 1376.7 J  $g^{-1}$  and 1248.3 J  $g^{-1}$ , increased remarkably compared to 598.3 J  $g^{-1}$  of pure AP. The rGO/MFe<sub>2</sub>O<sub>4</sub>  $(M = Cu, Co, Ni)$  nanohybrids demonstrate excellent catalytic effects in decreasing the HTD temperature and increasing the energy release of AP. However, the rGO/CuF nanohybrids showed the best catalytic effects and the rGO/NiF nanohybrids the least. The thermal catalytic performance of catalysts on the decomposition of AP is content dependent. As seen from Fig. 6, increasing the mass ratio of rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids in mixtures can decrease HTD peak temperature and the catalytic performance of rGO/CuF shows less relative to amounts compared to that of rGO/CoF and rGO/NiF nanohybrids.

For comparison, TG-DSC tests were further conducted to study the catalytic activity of the as-prepared MF ( $M = Cu, Co, Ni$ ) NPs and rGO sheets at a heating rate of 10  $^{\circ} \mathrm{C}$  min $^{-1}$ . As can be seen in

Table 2, rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids demonstrated better catalytic effect than that of pure NPs and rGO.

In Fig. 7a, there are two weight loss steps for pure AP, 23.1% of the first and 76.9% of the second. In Fig. 7b, two weight loss steps take place in all three mass ratio and the weight loss are almost the same, 35.5% of the first and 64.5% of the second. In contrast, Fig. 7c and d show that the weight loss of catalyst (5 wt%) is taken only in one step, which are consistent with their DSC results. Thus the mixtures (5 wt%) exhibit the best catalytic effects in decreasing the HTD temperature of AP compared to other mass ratio. However, for rGO/CuF, it is the most difficult to further decrease the HTD temperature of AP with addition of higher concentration.

### 3.3  $E_{a,\alpha}$  values of AP mixed with rGO/MFe<sub>2</sub>O<sub>4</sub> nanohybrids by model-free methods

To Evaluate the  $E_{a,\alpha}$  values of AP mixed with rGO/MFe<sub>2</sub>O<sub>4</sub> (3 wt%.) nanohybrids in the HTD process, mixtures were performed at heating rates of 5, 10, 15 and 20  $^{\circ}$ C min<sup>-1</sup>.

Table 2 Comparison of the catalytic activity of rGO, pure NPs with the rGO/MFe<sub>2</sub>O<sub>4</sub> in the HTD process of  $AP^a$ 

Catalyst	$\Delta T$ (°C)
CuFe <sub>2</sub> O <sub>4</sub>	71.5
CoFe <sub>2</sub> O <sub>4</sub>	45.4
NiFe <sub>2</sub> O <sub>4</sub>	38.2
rGO	0.9
rGO/CuFe <sub>2</sub> O <sub>4</sub>	95.6
rGO/CoFe2O <sub>4</sub>	86.4
$rGO/N$ iFe <sub>2</sub> O <sub>4</sub>	59.9

 $a$  T: decreased HTD peak temperature.



Fig. 7 TG curves of (a) pure AP, AP mixed with (b) rGO/CuF, (c) rGO/CoF and (d) rGO/NiF (1 wt%, 3 wt%, 5 wt%) nanohybrids.



Fig. 8 The curves of ln( $\beta$ <sub>i</sub>) by 1000/T<sub>a</sub> for thermal decomposition of (a) pure AP, AP mixed with (b) rGO/CuF, (c) rGO/CoF and (d) rGO/NiF (3 wt%) nanohybrids.



**Fig. 9** The curves of  $\ln\left(\frac{\beta_i}{T_{\alpha}^2}\right)$ by 1000/ $T_\alpha$  for thermal decomposition of (a) pure AP, AP mixed with (b) rGO/CuF, (c) rGO/CoF and (d) rGO/NiF (3 wt%) nanohybrids.

Two model-free methods, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) were applied for obtaining  $E_{a,\alpha}$ values.<sup>26-33</sup> The two methods allows the activation energy to be evaluated without making any assumptions about the reaction model. Therefore, for the first order reaction, extent of reaction conversion  $(\alpha)$  is calculated using the following eqn (1):



Table 4 The HTD  $E_{a,\alpha}$  values of pure AP and AP mixed with rGO/ MFe2O4 (3 wt%) nanohybrids by KAS method





Fig. 10 Dependence of  $E_{a\alpha}$  with  $\alpha$  according to (a) FWO method, (b) KAS method for the decomposition of AP mixed with rGO/MFe<sub>2</sub>O<sub>4</sub> nanohybrids.

$$
\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{1}
$$

The  $m_0$  and  $m_t$  are the mass of the sample at the starting and ending time; while  $m_\infty$  is the mass at arbitrary time or temperature.

The FWO method shown in eqn (2) is:

$$
\ln(\beta_i) = \text{const} - 1.0518 \frac{E_{a,\alpha}}{RT_{\alpha}} \tag{2}
$$

The KAS method shown in eqn (3) is:

 $\ln\left(\frac{\beta_i}{T_{\alpha}^2}\right)$  $\bigg) = \text{const} - \frac{E_{\text{a},\alpha}}{RT_{\alpha}}$ (3)

where  $\beta_i$  is heating rate,  $E_{a,\alpha}$  is activation energy, R is ideal gas constant,  $T_{\alpha}$  is temperature at arbitrary conversion values. Fig. 8 and 9 show the experimentally measured  $ln(\beta_i)$  versus 1000/ $T_{\alpha}$ and  $\ln \left( \frac{\beta_i}{T_{\alpha}^2} \right)$ ) versus  $1000/T_\alpha$  with rGO/MFe<sub>2</sub>O<sub>4</sub> nanohybrids, respectively.

The relationship of  $E_a$  to extent of conversion are calculated by FWO and KAS methods in HTD process. The  $E_a$  values and its corresponding linear correlation coefficient  $(R^2)$  for conversion values from 0.05 to 0.95, are shown in Tables 3 and 4. The dependence of  $E_a$  on  $\alpha$  using FWO and KAS method is shown in Fig. 10, respectively. Since the  $E_{a,\alpha}$  values of mixtures have increased, HTD process of AP is done harder and slower.

#### 3.4 Catalytic mechanism

According to the previous researches,<sup>34</sup> the first decomposition stage is solid–gas multiple reaction including decomposition and sublimation:

$$
NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^- \tag{4}
$$

$$
MF e_2 O_4 \rightarrow MF e_2 O_4 (h^+ + e^-) \tag{5}
$$

$$
Fe^{3+} + ClO_4^- \rightarrow Fe^{2+} + ClO_4 \tag{6}
$$

$$
Fe^{2+} + NH_4^+ \to Fe^{3+} + NH_4 \tag{7}
$$

$$
MFe2O4 (e-) + rGO \rightarrow MFe2O4 + rGO (e-)
$$
 (8)

Once the mixture of AP and  $rGO/MFe<sub>2</sub>O<sub>4</sub>$  is heated, electrons in the valence band (VB) of  $MFe<sub>2</sub>O<sub>4</sub>$  can jump to its conduction band (CB), meanwhile the generation of holes  $(h<sup>+</sup>)$  in the VB is coming. MFe<sub>2</sub>O<sub>4</sub> provide easy access to transfer electrons from  $ClO<sub>4</sub>^-$  to NH<sub>4</sub><sup>+</sup>. Because rGO are known as good electron acceptors,<sup>35</sup> the electrons are transferred to the rGO rapidly via a percolation mechanism.  $rGO/MFe<sub>2</sub>O<sub>4</sub>$  were used as catalysts for the decomposition, which can prevent the electrons and holes of  $MFe<sub>2</sub>O<sub>4</sub>$  recombining, and then boost the dissociation of ClO<sub>4</sub><sup> $-$ </sup>, thus leading to the enhanced catalytic effect.

### 4. Conclusion

 $rGO/MFe<sub>2</sub>O<sub>4</sub>$  (M = Cu, Co, Ni) nanohybrids have been successfully prepared by a facile hydrothermal way to prevent the agglomeration of NPs. The CuF, CoF, NiF NPs are homogeneously dispersed on rGO sheets. DSC results indicate that the rGO/CuF, rGO/CoF, rGO/NiF nanohybrids (3 wt%), can decrease the HTD peak temperature of pure AP from 424.7  $^{\circ}{\rm C}$  to 329.1 °C, 338.3 °C, 364.8 °C, respectively, and enhance catalytic performance with increasing amount. The two methods are used to estimate the values of  $E_a$  from TG tests without applying the model. Each activation energy has a separate value at different  $\alpha$ . According to the FWO method, the  $E_{a,\alpha}$  values ( $\alpha =$ 0.45) of AP with rGO/CuF, rGO/CoF, rGO/NiF nanohybrids are reduced from 159.37 kJ mol<sup>-1</sup> of pure AP to 79.05 kJ mol<sup>-1</sup>, 91.52 kJ mol<sup>-1</sup>, 116.76 kJ mol<sup>-1</sup>, respectively. As for the KAS method, the values are from 147.73 kJ mol<sup>-1</sup> to 68.64 kJ mol<sup>-1</sup>, 80.85 kJ mol<sup>-1</sup>, 116.76 kJ mol<sup>-1</sup>, respectively. The enhanced catalytic activity, attributed to the synergistic effect of NPs and rGO, can make the rGO/MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Co, Ni) nanohybrids be promising catalysts in the AP-based propellants or energetic materials.

There are no conflicts to declare.

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