Self-assembly preparation and thermal decomposition of Al/CuO/graphene oxide

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Abstract. Al/CuO/GO composite nanoenergetic materials were prepared by self-assembly. In this text, SEM, TEM, XRD, FTIR, XPS, TA-IR, TG-DSC were used to characterize Al/CuO/GO. The results show that the addition of graphene oxide decreased the initial reaction temperature of Al/CuO, indicating that graphene oxide promoted the reaction of Al/CuO. The exothermic energy of Al/CuO/GO (1 wt %) is 2089 J/g, which is 705 J/g higher than that of the Al/CuO without graphene oxide prepared by solvent ultrasonic method. When the content of graphene oxide exceeds a certain value, the increase of graphene oxide content will cause the decrease of reaction heat release of Al/CuO/GO. The results of thermal analysis infrared combined test show that graphene oxide promoted the reaction of Al/CuO.

1. Introduction
Graphene is a new two-dimensional material with a wide potential application prospect[1], which has many excellent properties. Graphene oxide (GO) is a derivative of graphene. There are epoxy, carboxyl and hydroxyl groups on basal plane and edge. These functional groups allow graphene oxide to become a site for self-assembly of other particles[2]. Thermite is a kind of energetic material widely applied, which plays an important role in special welding, propellant and explosives. In thermal decomposition progress, GO will release a large amount of heat[3]. Considering that there are many active sites on graphene oxide, the use of graphene oxide to realize the self-assembly of the thermite may have a positive impact on its performance.

In recent years, there have been some reports on the preparation of graphene based composite energetic materials and the study of the influence of graphene based materials on energetic materials[4]. Rajagopalan Thiruengadathan[5,6] used self-assembly method to prepare GO/Al/Bi2O3 nanocomposite particles, which showed an improvement to its combustion characteristics. Fe2O3/Al/graphene energetic nanocomposites were prepared by atomic layer deposition[7]. The characteristics of energy release and electrostatic discharge ignition of Fe2O3/Al/graphene energetic nanocomposites were studied. Also, Lan Yuan-Fei[8] prepared graphene aerogel/Fe2O3/AP nanostructured energetic composite and AP/Fe2O3/graphene nanocomposites, and studied the thermal properties of the related complexes.

In this paper, Al/CuO/GO energetic nano-composites with different contents of graphene oxide were prepared by self-assembly method. In polar solvents, metal particles and metal oxides are positively charged, and graphene oxide (GO) is negatively charged. Under the action of long-distance electrostatic force, graphene oxide sheets move to Al and CuO particles to realize self-assembly[9].
2. Experiment

2.1. Materials
Graphene oxide (GO) in the size range of 0.5-5.0 μm was purchased from Hangzhou hangdan photoelectric technology Co., Ltd., China. Nano aluminum powders (120 nm) and nano copper (II) oxide (200 nm) were purchased from Shanghai Xianxin new material technology Co., Ltd., China. Isopropyl alcohol (IPA, chromatographic grade) and N,N-dimethylformamide (DMF, chromatographic grade) were purchased from Aladdin reagent.

2.2. Preparation of nAl/CuO/GO energetic nano-composites
The self-assembly method was used to prepare Al/CuO/GO energetic composite materials. Graphene oxide is well dispersed in N,N-dimethylformamide (DMF), while nano Al powder is well dispersed in isopropanol. Therefore, the mixed solvent of DMF and IPA with a volume ratio of 1:1 is selected.

Here, we prepared Al/CuO/GO energetic composite materials, in which the mass percentage of graphene oxide was 0%, 0.5%, 1%, 3%, 5% and 10%, respectively. The equivalent ratio of fuel Al to oxidant CuO is 1.4 times of the stoichiometric ratio.

GO was dissolved in DMF for ultrasonic dispersion for 30 minutes. Meanwhile, nano Al powders and CuO particles were respectively dissolved in DMF/IPA mixed solvent for 30 minutes ultrasonic dispersion. Then, the well dispersed Al were added into graphene oxide solution, and ultrasonic dispersion was continued for 30 minutes. Subsequently, well dispersed CuO was added into the solution in the previous step, and ultrasonic dispersion was performed for 30 minutes. After ultrasonic dispersion, take out the samples and leave them for 24 hours. In this paper, Al/CuO without graphene oxide was prepared as the contrast sample. All samples prepared in the text needed to be left alone, and then the samples were put into a vacuum drying oven at 60°C for 24 hours.

2.3. Characterization
A field emission scanning electron microscopy (SEM, JSM-7001F, accelerating voltage 20 kV, Electronics, Japan) and a transmission electron microscope (TEM, H-7650, accelerating voltage 80 kV, Hitachi, Japan) were used to observe the morphology and structure. The FTIR spectrum was measured by using a TENSOR II FTIR Spectrometer (scanning range: 4000-500 cm⁻¹, Bruker, Germany). X-ray diffraction (XRD, Bruker, Germany) patterns were recorded on a D8 Advance X-ray diffractometer operated at 36 kV and 20 mA using a copper X-ray radiation (λ= 1.540598 Å). Samples were scanned from 5° to 80° with a step of 0.01° with a scanning speed of 5°/min. Thermogravimetric-differential scanning calorimetry analysis (TG-DSC) was performed on a TGA/DSC synchronous thermal analyzer (Mettler Toledo, Switzerland) to measure the weight loss and heat flow. The test was carried out under argon atmosphere (gas flow rate = 50 mL/min) at a heating rate of 20 °C/min from 50 to 900 °C. Elemental analysis was conducted on an X-ray photoelectron spectrometer (XPS) with an Al Ka anode (PHI Quantera II, ULVAC-Phi, Japan). The components of gaseous products were detected by STA 449F3 thermal analysis combined with infrared system (TA-IR, Netzsch, Germany) at a heating rate of 20 °C/ min from 50 to 900°C in argon. The flow rate of argon was 50 mL/min. The infrared spectrum scanning range was 4000-650 cm⁻¹, and the gas pool temperature was 200°C.

3. Results and discussion
Fig.1 shows the surface morphology of the products and raw materials prepared or used in the experiment. Fig.1(a) and (b) are SEM and TEM images of graphene oxide, respectively. It can be seen from Fig.1(a) and (b) that graphene oxide is a 2D planar structure. Fig.1(c) and (d) show the TEM diagram of nano CuO and Al. Compared to CuO, Al is more spherical and lighter in color. Fig.1 (e) and (f) are SEM and TEM images of Al/CuO/GO (5wt%) composite energetic respectively, which show that Al and CuO have been loaded on the graphene oxide film. Fig.1(g) is magnification of a part of (f). Fig.1(h) is the TEM diagram of the contrast sample Al/CuO. Compared Fig.1(g) with Fig.1(h), translucent GO, spherical Al and irregular spherical CuO can be seen clearly.
Fig. 1 SEM images of (a) GO and (e) nAl/CuO/GO (5 wt%), TEM images of (b) GO, (c) nano CuO, (d) nano-Al, (f) nAl/CuO/GO (5 wt%), (g) magnification of a part of (f), (h) Al/CuO

Fig. 2(a) shows the XRD curves of GO (pink), Al (red), CuO (blue) and Al/CuO/GO (5 wt%) (black). The (001) plane diffraction peak of GO appears at 10.56° [9]. According to the Bragg equation, it can be calculated that the lamellar spacing of GO is about 8.42 Å, which is larger than that of flake graphite (3.44 Å). The XRD curves of Al have four main peaks, 38.37°, 44.70°, 65.08° and 78.11°, corresponding to (111), (200), (220) and (311) crystal planes of Al [10], respectively. There are two distinct diffraction peaks of nano CuO at 35.54° and 38.69°, corresponding to the (-111) and (111) crystal planes of nano CuO respectively [11]. The XRD curves of Al/CuO/GO have five obvious diffraction peaks at 35.37°, 38.42°, 44.63°, 64.95° and 78.13°, corresponding to the crystal faces of CuO (-111), Al (111), Al (200), Al (220) and Al (311), respectively.

![XRD curves of GO, Al, CuO and Al/CuO/GO (5 wt%), FTIR curves of GO and Al/CuO/GO (5 wt%)](image)

The FTIR spectra of graphene oxide and Al/CuO/GO (5 wt%) are presented in Fig.2(b). There are absorption bands at 3389, 1727, 1622, 1398, 1218, 1052 cm\(^{-1}\) in the infrared curve of GO, corresponding to the stretching vibration of intermolecular hydrogen bond -OH, C=O stretching vibration, aromatic C=C stretching vibration, OH deformation vibration, epoxy group stretching vibration, alkoxy group stretching vibration, respectively [12]. The stretching vibration of aromatic C=C in graphene oxide appears at 1627 cm\(^{-1}\) in the infrared curve of Al/CuO/GO, which indicates the existence of graphene oxide in Al/CuO/GO energetic composites. The infrared peak at 586 cm\(^{-1}\) is corresponded to Cu-O bond, which indicates the existence of copper oxide in the composite [13].

In order to explore the possible chemical connection between graphene oxide and Al/CuO, XPS was used to test graphene oxide and Al/CuO/GO (5 wt%). Fig.3(a)-(d) shows the survey XPS spectrum, element composition, C 1s and O 1s spectrum of GO and Al/CuO/GO, respectively. As can be seen in Fig.3(a), graphene oxide has obvious peaks at 284.6 and 532.2 eV, corresponding to C 1s and O 1s, respectively, while Al/CuO/GO energetic composites have peaks near 74.0 and 932.6 eV,
corresponding to Al 2p and Cu 2p, respectively. The chemical composition of GO and Al/CuO/GO can be seen in Fig.3(b), which shows the ratio of C to O in graphene oxide is close to 2:1. The molar ratio of Al and CuO in Al/CuO/GO is about 0.86, which is close to 1.4 times of the stoichiometric ratio of Al/CuO (0.93). It can be seen in Fig.4(c) that the C 1s spectrum of Al/CuO/GO is obviously different from that of graphene oxide, which indicates that there may be electron transfer between graphene oxide and Al in the process of self-assembly. Four peaks can be obtained at binding energy 289.2, 288.4, 286.7 and 284.6 eV respectively, corresponding to O=C=OH, C=O, C-O-C/C-OH and C=C/C-C[14]. The C 1s spectra of Al/CuO/GO can also be divided into four peaks, which are O=C-O-Al of 288.8eV, C-O-C/C-OH of 286.7eV, C-O-Al of 285.7eV and C=C/C-C of 284.6eV. By comparing the C 1s spectra of graphene oxide and Al/CuO/GO, it can be seen that the new chemical interactions may be formed between Al/CuO and graphene oxide.

The O 1s region of graphene oxide can be divided into four peaks at 534.2, 532.9, 532.1 and 530.5.6 eV respectively, corresponding to physisorbed water, epoxy, C-OH and O=C-OH [5]. Six peaks at 534.2, 533.1, 532.2, 531.8, 531.2 and 530.0 eV can be obtained by fitting the O1s region of Al/CuO/GO, corresponding to oxygen in adsorbed water, epoxy, C-O-Al, C-OH, O=C=OH and Cu-O respectively. The shift of the spectrum may indicate the formation of new chemical bonds.

In order to explore the thermal decomposition of graphene oxide and Al/CuO/GO (5 wt%), the TA/IR test was carried out. The TG-DTA test curves of graphene oxide and Al/CuO/GO can be seen in Fig.4(a) and (b). As can be seen in Fig.4(a), the thermal decomposition of graphene oxide can be divided into three stages. The first stage is from 50 to 188.℃, in which the weight loss percentage of graphene oxide is about 19.7%, which may be caused by the escape of water and gas adsorbed and the mild decomposition of graphene oxide. The second stage is from 188℃ to 190℃, in which graphene oxide decomposes violently and releases a lot of heat, with a weight loss of 43.6%. The third stage is from 190 to 900℃. Weight loss in this stage is about 8.7%. When the temperature rises to 900℃, the residual weight of graphene oxide after decomposition is about 28.0%. It can be seen in Fig.4(b) that the mass percentage increased by 0.52% from 50 to 97℃, which is supposed to be caused by the formation of amorphous alumina on the surface of Al[15]. From 97 to 231℃ and from 231 to 397℃, there are two relatively obvious temperature ranges of mass loss for Al/CuO/GO. The percentage of mass loss is about 1.26% and 0.96%, respectively. From 397 to 900℃, the
decomposition is relatively gentle, and the weight loss is about 1.12%. It can be seen from Fig.4(b) that there is a very weak melting endothermic peak of nano aluminum particles at 642℃.

![Fig. 4 TG-DTA curves (a, b) of GO and Al/CuO/GO (5wt%)](image)

Fig. 5 Infrared absorption spectra of thermal decomposition products at different temperatures (a) GO and (b) Al/CuO/GO (5 wt%), curves of infrared absorption spectra of major products in the thermal decomposition versus temperature (c) GO and (d) Al/CuO/GO (5 wt%)

Fig.5(a) shows the infrared absorption spectra of the gasous products of GO. It can be seen from Fig. 5(a) that there are obvious infrared absorption peaks at 668, 1340, 2175 and 2359 cm⁻¹ for the decomposition products of graphene oxide at 197.22 ℃, while there are continuous burr-like infrared absorption bands from 1400 to 1750 cm⁻¹ and from 3500 to 3790 cm⁻¹. According to literature [16,17], the infrared absorption bands at 668, 1340 and 2359 cm⁻¹ correspond to the infrared absorption peaks of CO₂, the infrared band at 2175 cm⁻¹ corresponds to CO, and the continuous burr absorption band from 1400 to 1750 cm⁻¹, and from 3500 to 3790 cm⁻¹ correspond to gaseous H₂O. Compared with the infrared absorption signal of the decomposition products of graphene oxide at 197 ℃, the infrared absorption signal of the decomposition products of graphene oxide at 172 and 397 ℃ is weaker. It means that fewer gaseous products are formed at 172 and 397 ℃, whereas more gaseous products are formed at 172 ℃ than that at 397 ℃. Fig.5(c) shows the infrared absorption intensity of the main products of graphene oxide. It can be seen that the amount of CO and CO₂ rapidly increase to the
maximum value near 197 °C. With the increase of temperature, the amount of gas keeps in a low state and tends to be stable. Fig.5(b) shows the infrared spectra of decomposition products of Al/CuO/GO. It can be seen that the main products of Al/CuO/GO are CO₂ and vapours, corresponding to the infrared peaks at 2359 cm⁻¹ and the burr-like infrared bands from 1315 to 2017 cm⁻¹, and from 3480 to 3951 cm⁻¹, respectively. At 669 °C, products of Al/CuO/GO have the strongest infrared signal, while the products have the weakest signal at 99 °C. Fig.5(c) shows the curves of infrared intensity of CO₂ and gaseous H₂O produced by Al/CuO/GO. It can be seen in Fig.6(d) that the infrared absorption intensity of CO₂ decreases between 562 to 571 and 632 to 651 °C, while the temperature 571 and 651 °C is close to the peak temperature (571 and 649 °C) of the first and third exothermic peaks in the DTA curve of the Al/CuO/GO in Fig.4(b). It means that the decomposition process of graphene oxide may be affected by Al/CuO. Since the content of graphene oxide is small, the decomposition process is relatively mild and does not cause danger. The first exothermic peak of Al/CuO/GO is near 571 °C, which may be produced by the reaction between CuO and C[18]. The second exothermic peak is near 613 °C, which is lower than the melting point of nano Al particles (642 °C), and is generated by the solid-solid reaction of Al and CuO[19]. The third exothermic peak is around 649 °C, which is produced by the liquid-solid reaction between molten Al and CuO[20]. During the melting process of nano Al, the shell of alumina breaks, while the molten Al escapes from the shell and reacts with C and CO₂ produced by thermal deoxidation of graphene oxide. In addition, Fig.5(d) shows that gaseous H₂O appears a peak at 164 °C.

![Graph](image_url)

**Fig. 6 DSC (a) and TG (b) curves of Al/CuO with different contents of GO**

![Graph](image_url)

**Fig. 7 Parameters of reaction temperature (a) and energy release (b) as a function of GO proportion**

TG-DSC curves of Al/CuO at different GO contents are shown in Fig.6. It can be seen that under the condition of different graphene oxide content, the exothermic peak shape of Al/CuO is similar. The reaction heat release parameters of Al/CuO composite energetic materials with different graphene oxide content can be obtained. The detailed values of these parameters are shown in Fig.7. It can be seen from Fig.6(b) that the mass loss of Al/CuO caused by the temperature rise is very small. With the increase content of graphene oxide, the mass loss of Al/CuO/GO is also increasing.
Fig. 7(a) shows the change of initial reaction temperature ($T_{\text{onset}}$), exothermic peak temperature ($T_{\text{Peak}}$) and reaction termination temperature ($T_{\text{endset}}$) with different contents of graphene oxide. With the increase of graphene oxide content, the initial reaction temperature ($T_{\text{onset}}$) of Al/CuO decreased from 560°C (0 wt%) to 538°C (10 wt%). When the content of graphene oxide is between 0 and 3%, the $T_{\text{peak}}$ and $T_{\text{endset}}$ decrease, which indicates that appropriate amount of graphene oxide can promote the reaction between Al and CuO. However, when the content of graphene oxide continues to increase, the reaction between Al/CuO has not been further promoted, and $T_{\text{peak}}$ and $T_{\text{endset}}$ even increased. This result can also be obtained from Fig. 7 (b). As can be seen in Fig. 7 (b), when the content of graphene oxide is 0.5%, the reaction heat release is 2070 J/g, which is about 686 J/g higher than that of the sample without graphene oxide. Reaction heat release of Al/CuO with 1% graphene oxide is lower than its theoretical exothermic value (4144 J/g). Due to the strong activity of nano Al, inert Al$_2$O$_3$ shell cannot be avoided in the process of application, which will affect the reaction heat of the thermits. When the content of graphene oxide is 1% and 3%, the exothermic value of the sample is 2089 J/g and 2070 J/g respectively, which is close to that of the sample containing 0.5% graphene oxide. When the content of graphene oxide continues to increase to 5% and 10%, the reaction heat of the samples is 1813 J/g and 1156 J/g, respectively. The results show that excessive addition of graphene oxide will not further improve the reaction heat release of the sample.

4. Conclusion

Al/CuO/GO composite energetic materials with different graphene oxide content were prepared by self-assembly. The main products of thermal decomposition of Al/CuO/GO composite energetic materials are gaseous H$_2$O and CO$_2$, which may also have CO. The addition of graphene oxide decreased the initial temperature of exothermic reaction. When the content of graphene oxide is 1%, the exothermic energy of the Al/CuO/GO composite energetic material is the largest in the test samples, which is 705 J/g higher than that of Al/CuO without graphene oxide.

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