

# Preparation and Evaluation of Effective Combustion Catalysts Based on Cu(I)/Pb(II) or Cu(II)/Bi(II) Nanocomposites Carried by Graphene Oxide (GO)

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**Abstract:** In this work, the preparation and combustion catalysis effects of Cu<sub>2</sub>O–PbO/GO and CuO–Bi<sub>2</sub>O<sub>3</sub>/GO nanocomposites were systematically investigated. It was shown that the burning rate of the DB propellants can be significantly enhanced by both the nanocomposite catalysts, with reduced pressure exponent. In particular, the Cu<sub>2</sub>O–PbO/GO induced a burn rate enhancement for DB propellant in pressure range of 2–14 MPa, with the maximum catalytic efficiency of 3.87 at 2 MPa. More interestingly, it resulted in “mesa” burning of DB propellant in the

pressure range of 12–20 MPa ( $n = -0.05$ ). The CuO–Bi<sub>2</sub>O<sub>3</sub>/GO have the same effect with a burning rate increasing from 2.15 to 8.57 mm s<sup>-1</sup> at 2 MPa. Similarly, for the RDX-CMDB propellant, the GO-based composites of Cu<sub>2</sub>O–PbO/GO and CuO–Bi<sub>2</sub>O<sub>3</sub>/GO showed evident catalytic activities. Plateau combustion was achieved in their presence, which is of great importance for practical applications. The catalysis effects of the two composites are closely related to the high dispersion of metal oxide particles and GO with excellent thermal conductivity.

**Keywords:** Combustion catalysts • nano additives • Graphene oxide • Burning rate • Catalytic efficiency

## 1 Introduction

Graphene is a two-dimensional material with honeycomb lattice structure, which has a large theoretical specific surface area (SSA), high electrical conductivity, and excellent thermal conductivity [1, 2]. The metals/metal oxides and graphene can be combined into composite catalysts, where graphene plays a dual role of as a catalyst and a carrier [3]. The nanosized metal compounds can be well dispersed on the surface of graphene, greatly increases the catalytic performance due to synergistic and complementary effects [4]. In particular, they have a significant catalytic effect on the combustion of solid propellants [5]. These materials can increase the energy-release rate of solid propellants, resulting in higher the burning rates [6]. At the same time, the mechanical properties and the sensitivity of the propellants to impact and friction can be improved by using graphene or graphene oxide (GO) [7].

The nanosized Ni/graphene and Mn<sub>3</sub>O<sub>4</sub>/graphene nanocomposites were found to have strong catalytic effects on thermal decomposition of ammonium perchlorate (AP). By using 1 wt % of Ni/graphene, the catalytic effect would achieve its maximum, resulting in only one-step decomposition of AP with a peak temperature ( $T_p$ ) decrease of 97.3 °C [8]. Mn<sub>3</sub>O<sub>4</sub>/graphene showed a similar catalytic effect on AP decomposition, where  $T_p$  was reduced by 141.9 °C, due to significant synergies of Mn<sub>3</sub>O<sub>4</sub> and graphene [9]. In comparison to graphene, GO has functional groups on its surface, including carboxyl, epoxyl and hydroxyl groups, which could

combine GO with various substances by either covalent bonding or physisorption. In terms of catalysts, it has been reported that the CuO/GO nanocomposites prepared from water/isopropanol solvent are very effective in catalyzing AP decomposition and combustion [10]. In addition, if some energetic functional groups were introduced to GO, its catalytic activity and energy density would be significantly improved. For instance, nitrated GO makes  $T_p$  of AP decomposition to decrease by 106 °C, while the decomposition

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heat was increased from 875 to 3236 J g<sup>-1</sup> [11]. The Al/Bi<sub>2</sub>O<sub>3</sub> nanothermite could be deposited on functionalized graphene sheets using a self-assembly method [12]. A covalent bonding between Al and GO was observed, although no covalent bonding between Bi<sub>2</sub>O<sub>3</sub> and GO exists. The GO/Al/Bi<sub>2</sub>O<sub>3</sub> nanocomposites have excellent fuel/oxidizer contact and better heat transfer in comparison to randomly mixed Al/Bi<sub>2</sub>O<sub>3</sub>, resulting in enhanced reactivity and energy release from 739 J g<sup>-1</sup> to 1421 J g<sup>-1</sup>.

In terms of safety, the impact sensitivity of energetic materials (EMs) could be improved by graphene or GO due to improved heat conductivity and mechanical strength. A nanocomposite based on AP and graphene aerogels (AP/GA) was prepared by a sol-gel method [13], and the AP/GA nanocomposite has many voids with SSA of 49.18 m<sup>2</sup> g<sup>-1</sup>. About 94 wt-% of AP nanoparticles (69.4 nm) was attached to the skeleton of graphene. Based on AP/GA nanocomposites, a novel GA/Fe<sub>2</sub>O<sub>3</sub>/AP nanostructured energetic material was prepared, showing an open wedge-shaped meso-porous structure [14]. Except for AP, GA can also be used to prepare nanocomposites of ammonium nitrate (AN) [15]. The surfaces of unmodified HMX crystals are smooth and clean, while some wrinkles are observed in composite HMX/GO, which significantly improved the sensitivity of HMX [16]. Similarly, the addition of GO or reduced GO enhanced the decomposition of  $\epsilon$ -CL-20/glue formulation with a remarkable improvement in the heat release, and much lower mechanical sensitivity [17].

Therefore, the GO-based additives would function as catalysts and desensitizers [16–18]. As proved by many researchers, the nanosized bimetallic oxide composite catalysts were much better than the single metal oxides [19]. The catalytic effects of the bimetallic oxides could be further improved by introducing GO as a carrier [20–22]. This research paper intends to present the detailed preparation method for GO-based Cu<sub>2</sub>O–PbO and CuO–Bi<sub>2</sub>O<sub>3</sub> nanocomposites, which were further evaluated as the main catalysts of double-base propellants (DB) and RDX modified double-base propellants (RDX-CMDB). Emphasis would be paid for the effect of experimental conditions on the structure of the GO-based nanocomposites, as well as their catalytic effects on the decomposition and combustion of RDX-based propellants.

## 2 Experimental Section

### 2.1 Preparation of GO-Carried Composite Catalysts

**Preparation of Cu<sub>2</sub>O–Bi<sub>2</sub>O<sub>3</sub>/GO nanocomposite:** 850 mg of stoichiometrically pure Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 600 mg of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were placed in round flask, and dissolved with 50 ml diluted nitric acid using ultrasonic vibration. Take 200 mg of GO powder, which can be dispersed in a beaker by deionized water, adding 5 ml of polyethylene glycol-400 (PEG-400) as a surfactant. Then, the above-mentioned

Bi(NO<sub>3</sub>)<sub>3</sub>/Cu(NO<sub>3</sub>)<sub>2</sub> in nitric acid solution was added to the GO dispersion, stirring at room temperature for 1 h. Adjust the pH value of this mixture to 10.5 by dropwise addition of a diluted sodium hydroxide solution, and then continue stirring at room temperature for another 1 h. Later on, mix the resulted mixture for 1 h at 65 °C. The final precursor was filtered, washed, dried and grinded, and then subjected to calcinations for 2 h at 250 °C under nitrogen, yielding Cu<sub>2</sub>O–Bi<sub>2</sub>O<sub>3</sub>/GO composite nanopowder.

**Preparation of CuO–PbO/GO nanocomposites:** 860 mg of lead nitrate and 800 mg of copper nitrate were added to 50 ml of 1.0 mol L<sup>-1</sup> nitric acid, forming a mixed solution. Add 200 mg of GO powder in a beaker, and disperse it with distilled water by 1 h sonication. Then, 5 ml of PEG-400 was added and the mixture was stirred until a uniform dispersion was obtained. The mixed Pb(II)/Cu(II) nitrate solution was slowly added to this dispersion under stirring at room temperature. Then stir it for 1.5 h and keep it without stirring for 2 h. Next a 5% NaOH solution was added to adjust the pH value to 10. After another 1.5 h of stirring, the resulting mixture was heated up to 65 °C with stirring for 1 h, followed by a standby of about 1 h. Finally, it was subject to filtering, washing and drying. It was calcimined at 350 °C for 2 h under nitrogen atmosphere to yield the final nanocomposite product.

### 2.2 Preparation of Propellants Containing GO-based Nanocomposites

The DB propellants composed of 59% nitrocellulose (NC, 12.0%N content) and 30% nitroglycerine (NG), 8.5% of diethyl(o)-phthalate (DEP), 2% of dinitrodiphenylamine and 0.5% of vaseline. The composite modified DB propellant contains 36% of NC, 27% of NG, 26% of RDX, 2% of dinitrodiphenylamine, 3% of DINA, and 3% of other additives. For both the DB and CMDDB formulations, the catalysts were additionally introduced. The formulations are listed in Table 1.

As shown in Table 1, the content of the GO-based combustion catalysts is about 3 wt% for each sample. The samples were prepared by a conventional solvent free extruding method. The target-line method was used to determine the burning rate, where the strands were machined to a cylinder shape with dimensions of 5 × 150 mm and coated 6 times with polyvinyl alcohol solution. The initial ambient temperature was 20 °C and the applied pressure range was 2–20 MPa.

### 2.3 Characterizations

**Powder X-Ray Diffraction (PXRD):** A Bruker D8 was used to analyze the phase structure of the GO-Based catalysts, where the test conditions are as follows: Cu target ( $\lambda =$

**Table 1.** Formulations of the double-base (DB) and modified DB (MDB) propellants containing GO-based nanocomposites (in mass percent-age, %).

Samples	NC	NG	DEP	C <sub>2</sub>	Vaseline	Catalysts
DB	59	30	8.5	2.0	0.5	0
DB/GO	57	29	8.5	2.0	0.5	GO (3.0)
DB/nPCC	57	29	8.5	2.0	0.5	Cu <sub>2</sub> O–PbO (3.0)
DB/(Cu–Pb/GO)	57	29	8.5	2.0	0.5	Cu <sub>2</sub> O–PbO/GO (3.0)
DB/(Cu–Bi/GO)	57	29	8.5	2.0	0.5	CuO–Bi <sub>2</sub> O <sub>3</sub> /GO (3.0)
	NC + NG	RDX	C <sub>2</sub>	DINA	Others	
CMDB	66	26	2.0	3.0	3.0	0
CMDB/GO	63	26	2.0	3.0	3.0	GO (3.0)
CMDB/nPCC	63	26	2.0	3.0	3.0	Cu <sub>2</sub> O–PbO (3.0)
CMDB/(Cu–Pb/GO)	63	26	2.0	3.0	3.0	Cu <sub>2</sub> O–PbO/GO (3.0)
CMDB/(Cu–Bi/GO)	63	26	2.0	3.0	3.0	CuO–Bi <sub>2</sub> O <sub>3</sub> /GO (3.0)

0.15418 nm); tube voltage, 40 kV; current, 40 mA; scan range: 15 to 80 deg; scanning speed, 3 deg min<sup>−1</sup>.

**Transmission Electron Microscopy (TEM):** JEM-2010 equipment (200 kV) was used to determine the surface structure of the materials, which were dispersed in ethanol by sonication, and then deposited on a copper grid substrate.

**FTIR analysis:** The samples were mixed with KBr uniformly, and made into transparent thin films for measurement.

### 3 Results and Discussion

#### 3.1 The Experimental Conditions on the Structure of GO-based Nanocomposites

##### 3.1.1 The Effect of GO Concentration

The preparation of GO-based nanomaterials with bi-metallic oxides is more complicated than with single metal oxides, because the precipitation conditions should be fulfilled for both metal ions. As shown by various experimental attempts, a combined impregnation and liquid-phase chemical deposition method could be used for preparation of the CuO–Bi<sub>2</sub>O<sub>3</sub>/GO and Cu<sub>2</sub>O–PbO/GO nanocomposites.

The concentration of the dispersed GO in H<sub>2</sub>O is limited to a certain level (e.g. 1.0 mg/mL). In order to check the effect of GO concentration on the structure of the final nanocomposites, different amounts of metal salts could be used with the same concentration of GO. Herein, five different mass ratios (1:1, 1:2, 1:3, 1:4 and 1:5) of PbO–Cu<sub>2</sub>O/GO have been attempted. It has been shown from XRD and SEM analysis that, in general, by increasing the metal salts concentration, the amount of PbO–Cu<sub>2</sub>O deposited on GO was increased greatly (Figure S1, ESI). When the mass ratio of GO and metal oxides was less than 1:3, agglomeration occurred. When the ratio is 1:3, the particle size of PbO–Cu<sub>2</sub>O is about 50 nm without obvious agglomeration.

Therefore, the optimal mass ratio between GO and metal oxides should be about 1:3.

##### 3.1.2 The Effect of pH Value on the Precursors

In the case of Cu<sub>2</sub>O–PbO/GO, six different pH values (8.0, 8.5, 9.0, 9.5, 10.0 and 10.5) were applied to prepare its precursor, which was characterized by SEM and P-XRD techniques. As shown in Figure S2, with the increase of the pH value, the amount of precipitation on the GO surface was increased, but the particle size was decreased. When the pH value was 9.5, the particle size is in a narrow range of 50–60 nm with round shape, while it is about 100–200 nm with irregular shape for pH value of 8.0. However, when the pH value is over 10.0, a more severe agglomeration would occur due to stack of GO flakes. In general, a higher pH value is in favor of more precipitation at a higher speed. As shown from P-XRD analyses (Figure S3), with the increase of the pH value, the peak intensity would be greatly enhanced due to more complete precipitation, resulting in a higher content of Cu<sub>2</sub>O–PbO after calcination. Therefore, the optimal pH value could be 10.0 for preparation of Cu<sub>2</sub>O–PbO/GO.

It is also the case for CuO–Bi<sub>2</sub>O<sub>3</sub>/GO. After several experiments using pH values of 8.5, 9.5, 10.5, 11.5 and 12.5, we found that 10.5 could be the best choice for this nanocomposite due to the highest metal content with promising particle size (40 nm). As shown in Figure S4, when the pH value was 8.5, the metal hydroxides deposited on GO were scarce with average particle size of 20 nm. With the increase of the pH value, the particle size was increased with a maximum value of 400 nm (pH = 12.5), which is opposite to that of Cu<sub>2</sub>O–PbO/GO.

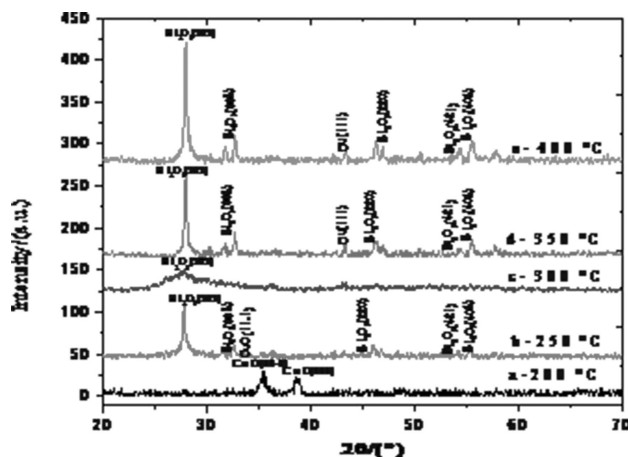
##### 3.1.3 The Effect of Calcination Temperature

After the preparation of the metal hydroxides/GO as the precursors, the calcination process is the key process to

control the structure of the final nanocomposites. By keeping the other experimental conditions unchanged, the effect of calcination temperature on the structure of the final nanocomposites was investigated. In the case of  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$ , the calcination temperature was selected to be 250 °C, 300 °C, 350 °C, 400 °C, and 450 °C.

The PXRD spectra of samples prepared at different calcination temperatures are shown in Figure S5, when the temperature was 250 °C. There are only two weak diffraction peaks at 36.358° and 42.237°, which could be assigned to cubic  $\text{Cu}_2\text{O}$  (PDF#05-0667), but no characteristic peaks of PbO were found. Figure S5 (b) is obtained at a calcination temperature of 300 °C, which has two diffraction peaks at 28.633° and 31.831°, indexed as (101) and (110), respectively. It is due to the presence of tetragonal PbO (PDF#05-0561), indicating that this temperature is sufficient to form PbO. Meantime, the characteristic diffraction peaks of  $\text{Cu}_2\text{O}$  are also shown in the spectrum. When the calcination temperature is 350 °C, two peaks at 43.297° and 50.433° are shown, which could be indexed as (111) and (200), in agreement with Cu elemental standard peaks (PDF#04-0836). It reveals that, the calcination temperature is high enough to reduce  $\text{Cu}_2\text{O}$  to Cu by the carbon in GO. Therefore, the peaks for PbO were enhanced, but the peaks for  $\text{Cu}_2\text{O}$  were weakened. This phenomenon was more obvious at a calcination temperature of 400 °C, where the characteristic peaks of elemental Cu were enhanced. At a calcination temperature of 450 °C, the characteristic peak of  $\text{Cu}_2\text{O}$  disappeared, while the  $\text{Pb}_3\text{O}_4$  crystal was detected according to its standard spectrum (PDF#08-0019). Therefore, in order to get PbO/ $\text{Cu}_2\text{O}$  nanocomposites, ensuring that  $\text{Cu}_2\text{O}$  would not be reduced to Cu, the calcination temperature should be around 300 °C for the preparation of  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$ .

In the case of  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$ , the attempted temperatures were 250 °C, 300 °C, 350 °C, 400 °C, and 450 °C. Figure 1 shows the PXRD spectra of different  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  nanocomposites prepared at these temperatures. As shown in Figure 1a, the diffraction peaks at 35° and 38° are due to the presence of cubic CuO crystals (PDF#48-1548), which means that copper hydroxide has been decomposed into CuO at 200 °C. However, there is no characteristic peak for bismuth oxide, which indicates that the bismuth hydroxide has not been decomposed at this temperature. When it was calcined at 250 °C, the peaks at 27°, 32°, 46°, 46°, 54°, 55°, 57° corresponding to monoclinic  $\text{Bi}_2\text{O}_3$  (PDF#65-1209) appear. Meantime, the peaks for cubic CuO are also present. It means that the calcined product is mainly  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  at this temperature. In case of calcination at 300 °C, the diffraction peaks for  $\text{Bi}_2\text{O}_3$  become wide and disperse, indicating the poor crystallinity of  $\text{Bi}_2\text{O}_3$ . Also there is no CuO shown due to its reduction into  $\text{Cu}_2\text{O}$  and Cu. As the temperature was further elevated, only Cu could be observed. Therefore, the optimum calcination temperature is about 250 °C.

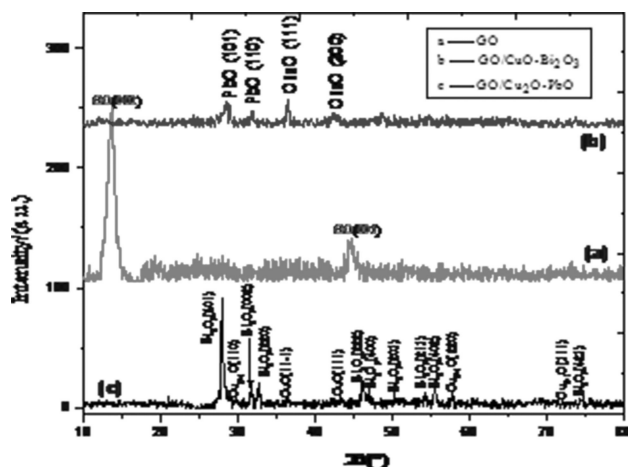


**Figure 1.** PXRD spectra of different  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  nanocomposites prepared at various calcination temperatures (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 350 °C and (e) 400 °C.

## 3.2 Morphology and Structure of GO-based Nanocomposites

### 3.2.1 Phase Analysis by Powder X-ray Diffractometry

Using the most appropriate experimental conditions summarized above, high-purity  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  and  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  nanocomposites were prepared. Their phase purity and crystal structures were determined by powder X-ray diffractometry, and presented in Figure 2.



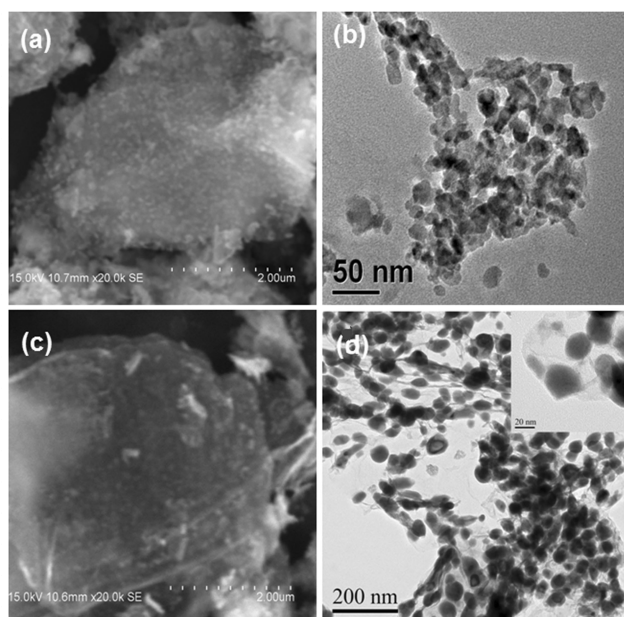
**Figure 2.** Powder X-ray spectra of pure GO (a),  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  (b) and  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  (c) nanocomposites

As shown in Figure 2, for the  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  nanocomposite, the peaks at 28°, 31°, 48° and 54° correspond to the indexed plane (101), (110), (112) and (211) of PbO, respectively, according to the standard pattern (PDF#05-0561). The diffraction peaks at 36.358° and 42.237°, 61.284°

and  $73.466^\circ$  could be assigned to indexed planes of (111), (200), (220) and (311), based on the standard XRD spectrum of cubic  $\text{Cu}_2\text{O}$  (PDF#05-0667). The above results indicate that the product is phase-pure nanocomposite of  $\text{PbO}/\text{Cu}_2\text{O}/\text{GO}$ . Comparing the PXRD patterns of graphite oxide (a) and  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  (b), as stated in Section 3.1.3, the peaks at  $27^\circ$ ,  $32^\circ$ ,  $46^\circ$ ,  $46^\circ$ ,  $54^\circ$ ,  $55^\circ$ ,  $57^\circ$  of  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  correspond to the monoclinic  $\text{Bi}_2\text{O}_3$ . And the peaks at  $35^\circ$  and  $38^\circ$  are due to cubic  $\text{CuO}$ . In addition, it is worth noting that the (002) plane was significantly decreased for GO due to deposition of  $\text{CuO}$  and  $\text{Bi}_2\text{O}_3$  crystals and exfoliation of graphite oxide.

### 3.2.2 Morphology Analyses by SEM/EDS and TEM Techniques

The SEM and TEM images of  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  and  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  nanocomposites are shown in Figure 3. The edge contour of two staggered  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  sheets can be clearly seen, which indicates that it is easier to be exfoliated after deposition of the metal oxides. The SEM image show that the particle size distribution on GO is narrow and the average particle size is about 40 nm for  $\text{CuO}-\text{Bi}_2\text{O}_3$ , which was uniformly dispersed on the surface GO with slight agglomeration.



**Figure 3.** SEM and TEM images of  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  (a, b) and  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  (c, d) nanocomposites

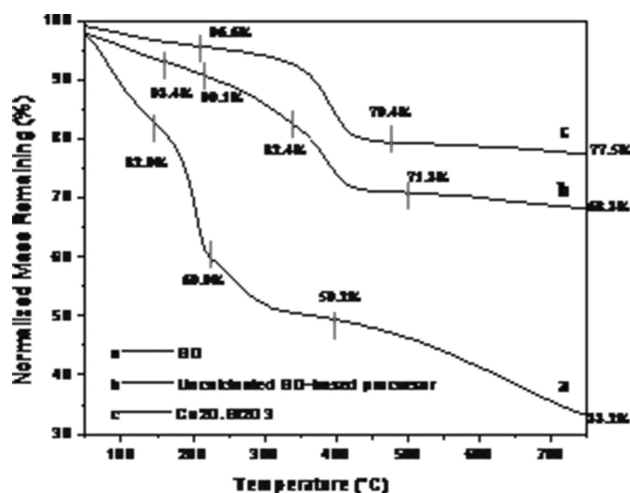
The above proposition was further supported by TEM images, which clearly shows the morphology of the particles in the nanocomposite, where the  $\text{CuO}-\text{Bi}_2\text{O}_3$  particles are spherical with particle size ranging from 20 to 50 nm. As

for the  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  nanocomposite, it can be seen that more spherical  $\text{Cu}_2\text{O}-\text{PbO}$  with larger particle sizes are dispersed on the GO surface. We can also see that the particles are evenly dispersed on the surface of GO without any agglomeration, and the particle size is about 40 nm. In order to further determine the composition of the nanocomposites, the samples were analyzed by EDS (see Figure S6). In the case of  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$ , four kinds of elements C, O, Cu and Pb were detected, where the Pb content is the largest, reaching 51.59%. Since the atomic ratio of Pb/O is 1:1 for  $\text{PbO}$ , the oxygen contribution from this component should be about 8.90%. The measured mass content of Cu is 17.22%, while atomic ratio of Cu/O is 2:1, so the atomic percentage of copper oxide containing oxygen is 9.68%, the remaining 15.61% of the oxygen should be from GO due to oxygen containing functional groups such as  $-\text{OH}$  and  $-\text{COOH}$ . Apparently, in this nanocomposite, the catalyst load, namely the  $\text{Cu}_2\text{O}-\text{PbO}/\text{GO}$  ratio, can reach 3.24/1. It is also the case for  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$ . As can be seen from Figure S6, the sample contains only four elements: C, O, Cu and Bi. It reveals that the total metal oxides load to the substrate GO is about 3.16/1.

### 3.2.3 Thermal Decomposition Properties

Herein, the  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  was taken as an example to show the thermal degradation properties of this kind of nanocomposite. Figure 4 presents the TG curves of the graphite oxide (a), the precursor without calcination (b) and  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  nanocomposite (c) under dynamic nitrogen atmosphere.

It has been shown that at least three decomposition steps could be observed for pure graphite oxide due to loss of oxygenated functional groups. The solid residue is about 33.2% for this carbon material. As shown in Figure 4, the



**Figure 4.** TG curves of graphite oxide (a), GO-based precursor (b) and  $\text{CuO}-\text{Bi}_2\text{O}_3/\text{GO}$  nanocomposite (c) under nitrogen atmosphere



mass of the two nanocomposite samples remains constant above 450 °C, revealing complete decomposition and the composition of their residues reaches equilibrium. The residual mass fraction for CuO–Bi<sub>2</sub>O<sub>3</sub>/GO nanocomposite is 77.5%. The mass losses are because of the removal of oxygenated functional groups on GO flakes. For the precursor, the residual mass fraction is about 68.3%. During its calcination process (it is 250 °C for CuO–Bi<sub>2</sub>O<sub>3</sub>/GO), the metal hydroxide transformed into oxides with H<sub>2</sub>O losses and the functional groups on GO were also removed. However, due to the presence of these metal oxides, the oxygenated functional groups on GO are stabilized, thus resulting in the increase of onset temperature for decomposition from 160 °C to 340 °C. By comprehensive analysis, the mass ratio of GO/CuO–Bi<sub>2</sub>O<sub>3</sub> is about 1:3, fitting well with original elemental design of this nanocomposite catalyst.

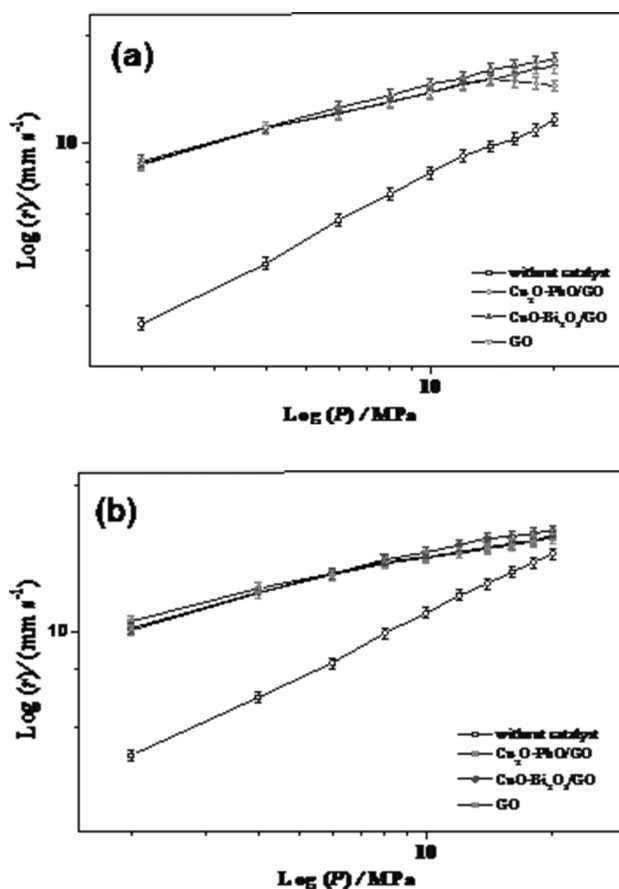
### 3.3 Catalytic Effects on Combustion of DB and RDX-CMDB Propellants

#### 3.3.1 The Catalytic Effects on Burning Rates

The burning surface of a rocket propellant grain recedes in a direction perpendicular to itself. The rate of regression, typically measured in mm s<sup>−1</sup>, is termed the burning rate (or burn rate,  $r$ ). Knowing quantitatively the burning rate of a propellant, and how it depends on various conditions, is fundamentally important for a successful design of a solid rocket motor. There are various factors that influence the burning rate, and the most significant ones are: (1) combustion chamber pressure “ $p$ ”; (2) the initial temperature of the propellant grain; (3) the velocity of the combustion gases flowing parallel to the burning surface; (4) the local static pressure; (5) motor acceleration and spin. The burning rate can be particularly sensitive to the value of the pressure exponent,  $n$ , which is the slope of the  $\log(r)$  vs.  $\log(p)$  curve. High values of  $n$  would produce large changes in the burning rate with relatively small changes in chamber pressure but with potentially catastrophic consequences. The efficiency factor  $\eta = r_c/r_0$ , where  $r_0$  is the burning rate of the blank reference propellant and  $r_c$  is the burning rate of the propellants with catalysts.

The catalytic effect of Cu<sub>2</sub>O–PbO/GO and CuO–Bi<sub>2</sub>O<sub>3</sub>/GO nanocomposite on combustion of DB and RDX-CMDB propellants was evaluated by standard strand burner experiments. The dependence of the burning rate on the pressure is shown in Figure 5 with the detailed data summarized in Table 2. It has been found that the burning rates of the propellants can be significantly enhanced with reduced pressure exponents by introducing both nanocomposite catalysts.

It was proved in the literature that the PbO/GO nano-additive is very effective in catalytic combustion [18]. When the PbO was combined with Cu<sub>2</sub>O, its catalytic efficiency was further improved. As shown in Figure 5 and Table S1,



**Figure 5.** Effect of GO-based nanocomposite catalysts on burn rate of DB propellants (a) and RDX-CMDB propellants (b).

Cu<sub>2</sub>O–PbO/GO induced a burning rate enhancement of DB propellant in pressure the range of 2–14 MPa with a maximum catalytic efficiency of 3.87 at 2 MPa. Under the effect of pure Cu<sub>2</sub>O–PbO nanocomposite, the burning rate at lower pressure (e.g. < 8 MPa) could be greatly improved, but such effect at higher pressure is very limited. With the dispersion and synergistic catalytic effect of GO, the burning rate at the full pressure range was significantly improved. The “mesa” burning occurred in the range of 12–20 MPa ( $n = -0.05$ ). In comparison, CuO–Bi<sub>2</sub>O<sub>3</sub>/GO can induce an accelerated combustion of DB propellant at 2 MPa, where the burning rate was increased from 2.15 to 8.57 mm s<sup>−1</sup> (3 times higher), with a maximum catalytic efficiency of 3.99. The plateau combustion occurred between 10–20 MPa, where  $n$  was reduced by more than 50% in comparison with the blank sample.

In the case of RDX-CMDB propellant, the catalytic combustion of GO-based nanocomposites was similar. As shown in Figure 5 and Table 2. It was also reported that the overall catalytic performance of PbO/GO on RDX-CMDB propellant is promising with burning rate increase from 3.09 to 6.88 mm s<sup>−1</sup> at 2 MPa [18]. The plateau combustion zone was observed at a pressure range of 10–20 MPa ( $n = 0.27$ ). For

**Table 2.** The burning rate of NC/NG DB and RDX-CMDB propellants under the effect of GO-based nanocomposites.

Samples	Burn rate ( $r$ in $\text{mm s}^{-1}$ ) at different pressure (in MPa)										Pressure range (MPa)	$n$
	2	4	6	8	10	12	14	16	18	20		
DB	2.15	3.19	5.20	6.49	7.81	8.99	9.77	10.30	11.22	12.24	10–20	0.619
DB/GO	8.42	11.40	12.88	14.31	15.38	16.55	17.20	17.99	18.96	19.20	10–20	0.326
DB/nPCC	5.72	6.56	6.07	6.64	7.51	8.43	9.39	10.55	–	–	10–16	0.723
DB/(Cu–Pb/GO)	8.33	11.41	12.96	14.19	15.46	16.68	17.33	17.04	16.66	16.35	12–20	–0.055
DB/S(Cu–Bi/GO)	8.57	11.47	13.57	15.04	16.60	17.40	18.73	19.39	19.94	20.51	10–20	0.311
CMDB	3.09	5.34	7.42	9.85	11.88	14.04	15.75	17.54	19.54	20.92	10–20	0.812
CMDB/GO	10.10	14.38	17.11	19.03	20.01	20.97	21.89	22.68	23.44	24.31	10–20	0.278
CMDB/nPCC	5.89	5.73	7.60	9.52	11.44	13.60	15.58	17.76	19.88	22.68	10–20	0.970
CMDB/(Cu–Pb/GO)	10.99	15.01	17.34	19.35	20.29	21.19	22.25	23.01	23.7	24.84	8–18	0.256
CMDB/(Cu–Bi/GO)	10.29	14.46	17.27	19.77	21.14	22.66	24.21	24.52	25.37	25.97	8–20	0.299

Note: nPCC denotes the  $\text{Cu}_2\text{O}$ – $\text{PbO}$  nanocomposite.

the  $\text{Cu}_2\text{O}$ – $\text{PbO}$ /GO nanocomposite, the catalytic efficiency was much better than that of pure  $\text{Cu}_2\text{O}$ – $\text{PbO}$ . The maximum catalytic efficiency in the pressure range of 2–14 MPa was 3.56, while the corresponding plateau combustion occurred at 8–18 MPa ( $n=0.26$ ). In comparison, the addition of  $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO increased the burning rate by 233% (3.09 to  $10.20 \text{ mm s}^{-1}$ ) at 2 MPa with a maximum catalytic efficiency of 3.33 and a plateau combustion zone of 14–20 MPa ( $n=0.21$ ). These two nanocomposite catalysts based on GO are promising for RDX-CMDB propellants. When compared with the pure metal oxides, the inclusion of GO would greatly improve the heat conductivity and the reactive sites of the catalyst due to better dispersion [23]. As reported in the literature [3], the GO itself is energetic and the heat release from the decomposition of GO could greatly improve the reaction rate at the burning surface. As one of the most important products from GO, functionalized graphene sheets (FGs) have been used in monopropellant nitromethane as well [24]. It was found that the ignition temperatures could be lowered while the burning rates increased when the FGs were included (i.e., > 175% increase).

Although many efforts have been devoted to evaluate the catalytic mechanisms of combustion catalysts, it is still not so clear how the nano additives could change the burning rate of the DB and CMDB propellants. In this work, it was proposed that the lead-based catalysts could short the decomposition course, and accelerate the exothermic rate of energetic matrix (NC/NG) of DB propellant [25]. According to previous reports, during the decomposition of NC/NG, the scission of O– $\text{NO}_2$  bond and the crosslink structure in NC/NG matrix was facilitated [26]. Thus, the amounts of  $\text{CH}_2\text{O}$ , CO and  $\text{CO}_2$  as the main gaseous products was increased in the presence of lead-based compounds, and the ratios of  $\text{CH}_2\text{O}/\text{NO}_2$  and  $\text{CO}/\text{NO}_2$  were also increased. Consequently, the heat-release rates were also increased due to the enhanced reaction rates, which thus result in enhanced heat feedback and higher burning rates. Combustion waves of the DB and CMDB propellants with different combustion catalysts were obtained at 2 MPa as shown in Figure S7. For

the DB propellants, the burning-surface temperatures were determined to be  $481^\circ\text{C}$ ,  $532^\circ\text{C}$  and  $610^\circ\text{C}$  for the samples without catalyst and with  $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO and  $\text{PbO}$ – $\text{Cu}_2\text{O}$ /GO, respectively. It is obvious that the existence of combustion catalysts results in higher burning-surface temperature, confirming the enhanced heat release near surface. Similar phenomena were observed for the RDX-CMDB propellants, the surface temperatures were  $594^\circ\text{C}$ ,  $611^\circ\text{C}$  and  $672^\circ\text{C}$  for the propellants without catalyst and with  $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO and  $\text{PbO}$ – $\text{Cu}_2\text{O}$ /GO, respectively. This also indicates the increased heat release near burning surface. Besides, GO could improve the burning rate of NC due to much faster heat conduction of GO flakes [26]. It was shown that the burning rate of NC could be significantly increased with the increase of GO content in GO/NC films (content of GO = 0.0–1.3 wt-%) [27].

As stated above, both the  $\text{Cu}_2\text{O}$ – $\text{PbO}$ /GO and  $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO nanocomposites are very effective in improving the combustion performance of DB and RDX-CMDB propellants. Specifically, mesa burning was achieved at 12–20 MPa for the DB propellant with  $\text{Cu}_2\text{O}$ – $\text{PbO}$ /GO as the catalyst. According to the literature, this is due to the inhibition reaction in the fizz zone caused by the lead or lead oxide derived from the nanocomposite [28]. Moreover, plateau burning, which is also favorable for practical applications, was observed for the DB propellant with  $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO and the RDX-CMDB propellants with different catalysts ( $\text{CuO}$ – $\text{Bi}_2\text{O}_3$ /GO and  $\text{PbO}$ – $\text{Cu}_2\text{O}$ /GO). It is noticed that the plateau burning exists at higher pressures than the super-rate burning, which originates from the enhanced conductive heat as a result of the formation of carbonaceous materials in the fizz zone and the enhanced heat flux. With the increase in burning rates at higher pressure, the formation of carbonaceous materials diminishes and thus super-rate burning diminishes to generate plateau burning [25].

## 4 Conclusions

The Cu<sub>2</sub>O–PbO/GO and CuO–Bi<sub>2</sub>O<sub>3</sub>/GO nanocomposites were prepared in this work. For Cu<sub>2</sub>O–PbO/GO with average particle size of 40 nm, the optimal experimental conditions are: metal oxides/GO of 3:1, soaking temperature of 65 °C, pH in 9.0–9.5 and calcination at 300 °C. As for CuO–Bi<sub>2</sub>O<sub>3</sub>/GO with average particle size of about 35 nm, the best conditions are: demulsification at 65 °C, m(GO):m(CuO):m(Bi<sub>2</sub>O<sub>3</sub>) = 1:0.75:2.25, pH value of 10.5, and calcination temperature of 250 °C.

The burning rate of the DB propellants can be significantly improved with reduced pressure exponent by both nanocomposites. In particular, the Cu<sub>2</sub>O–PbO/GO induced a burning rate enhancement of DB propellant in pressure range of 2–14 MPa with a maximum catalytic efficiency of 3.87 at 2 MPa and mesa burning was achieved. The CuO–Bi<sub>2</sub>O<sub>3</sub>/GO was also effective in improving the combustion of DB propellant. On the other hand, the addition of Cu<sub>2</sub>O–PbO/GO and CuO–Bi<sub>2</sub>O<sub>3</sub>/GO results in a plateau burning of RDX-CMDB propellants, favorable for their practical applications. The evident catalytic activities of the two nanocomposites are believed to be due to the highly dispersed metal oxide particles and GO with high thermal conductivity.

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