

2D COPPER HYDROXIDE ACETATE PLATES – A NOVEL ADDITIVE FOR ENHANCING THE THERMAL DECOMPOSITION PERFORMANCE OF AMMONIUM PERCHLORATE

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Abstract

Two-dimensional (2D) copper hydroxide acetate plates (CuHA) have been fabricated by a simple precipitation process. Their influence on the thermal decomposition of ammonium perchlorate (AP) was explored by thermogravimetry and differential scanning calorimetry. It was found that the in situ generated CuO strongly boosts the thermal decomposition performance of AP. In particular, the addition of 3 wt.% CuHA to AP lowers the decomposition temperature of the latter by 118 °C and, moreover, the heat release is increased almost twofold compared to that of pure AP.

Key words: ammonium perchlorate, thermal analysis, catalysis, copper hydroxide acetate, CuO

Introduction. As an oxidizer, ammonium perchlorate (NH_4ClO_4 , AP) is the main component of composite solid propellants [1]. The efficiency and burn rate of AP-based fuels strongly depend on the thermal decomposition performance of AP. Nanometer-sized transition metals, their oxides and composites have been widely adopted as catalysts to enhance the burning rate characteristics of AP [1]. These catalysts reduce the decomposition temperature of AP, simultaneously

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yielding higher heat release, thus improving its efficiency in the solid rocket propellants. Up to now numerous catalytic micro/nanoparticles with various sizes and morphologies have been reported. Very recently, the importance of sheet-like nanostructures toward AP thermal decomposition has been highlighted. These 2D materials have a higher surface area-volume ratio which leads to the improved transport of gas molecules and electron transfer, together with increased number of active sites. For instance, ZnO [2] and CuO [3] nanosheets have been successfully employed as catalysts to accelerate AP decomposition. Furthermore, BAO-YUN et al. [4] reported the promotional effect of 2D MOF material on the AP combustion. Very recently AN et al. [5] found that MgCo_2O_4 nanosheets exhibit excellent catalytic activity against AP-based energetic molecular perovskites, and ZHOU et al. [6] demonstrated that Prussian Blue ultrathin nanosheet assembly material greatly promotes the AP decomposition process.

The main goal of the present study is to introduce 2D copper hydroxide acetate plates as a novel highly efficient burning rate booster for AP thermal decomposition. Copper hydroxide acetate ($\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$, CuHA) is a lamellar organic-inorganic material which attracts attention in different areas of materials science because of its magnetic, catalytic, photocatalytic and cation-exchangeable properties [7]. Herein, CuHA nanoplates were successfully fabricated by a simple, rapid and scalable urea-assisted method and the as-formed product was characterized. The decomposition process in the CuHA/AP system was then studied using thermogravimetry and differential scanning calorimetry (TG-DSC) and the possible reaction mechanism was discussed.

Experimental. All the reagents (copper acetate monohydrate, urea, AP and anhydrous ethanol) were of analytical grade. The reaction of urea in copper acetate water solution was used to fabricate 2D CuHA plates. For this synthesis, 0.3 g of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$, 0.2 g of urea, and 50 mL distilled water were mixed in a 100 mL beaker and the resulting solution was heated at 90°C for 30 min on a plate under magnetic stirring. The hydrolysis of urea provides OH^- groups that react with the copper acetate. The as-formed greenish precipitate was thoroughly rinsed with water, filtered and dried at room temperature for 24 h.

The CuHA powder was characterized by X-ray diffraction (XRD, PANalytical Empyrean with $\text{CuK}\alpha$ radiation), scanning electron microscopy (SEM, JEOL 5510, applying gold coating), FTIR spectroscopy (Nicolet 6700, KBr pellets) and TG (TA650, N_2 atmosphere). The thermal behaviour of pure AP and CuHA-loaded samples was studied by TG and DSC (DSC250-TA) under N_2 atmosphere. AP was intermixed with CuHA by grinding in the presence of absolute ethanol in a mortar and dried at 60°C . Three samples denoted as CuHA-*X*/AP, where *X*=1, 2 and 3 indicates the weight percentage of CuHA, have been prepared.

Results and discussion. Firstly, the micromorphologies of the as-prepared particles were inspected by means of SEM (Fig. 1a). Results revealed the formation of rectangular plate-like crystals on the micrometer scale. Some of the plates

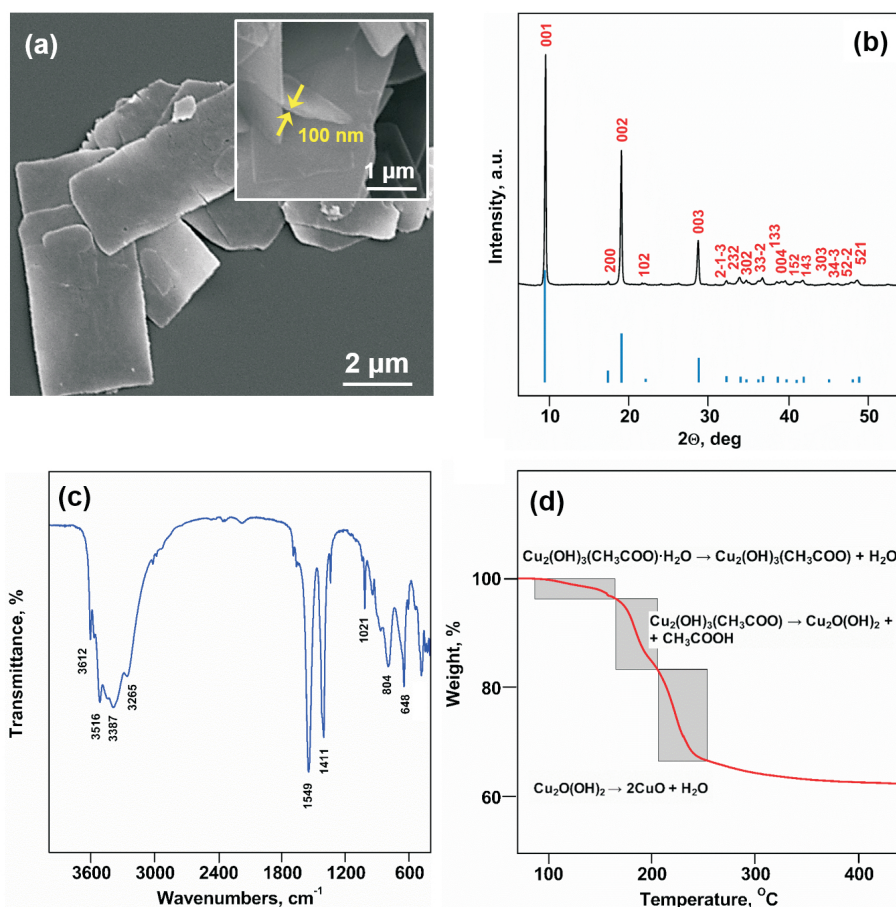


Fig. 1. (a) SEM, (b) XRD, (c) FTIR, and (d) TG results for CuHA

cross-stack with each other (see the inset) and their thickness is approx. 100 nm. As observable in Fig. 1b, the XRD pattern confirms the formation of pure monoclinic Cu₂(OH)₃(CH₃COO)·H₂O phase (PDF 00-058-0183). FTIR spectrum of the material, shown in Fig. 1c, provides the spectral fingerprints of CuHA. In particular, the bands in the region between 3000 and 3700 cm⁻¹ are attributed to matrix hydroxide groups and water, ν(-COO⁻) stretching vibrations appear at 1549 and 1411 cm⁻¹, while the bands at 648, 804 and 1021 cm⁻¹ can be assigned to the Cu-O-H bonds [8]. Finally, the thermal behaviour of CuHA nanoplates is demonstrated in Fig. 1d. The TG analysis shows that CuHA undergoes a three-stage decomposition process: the first stage (up to 165 °C) corresponds to the loss of the water molecules, the second stage (up to 204 °C), and the third stage (up to 250 °C) results from the complete thermal decomposition of CuHA to CuO [9].

In the DSC scan (10 °C min⁻¹) of the neat AP, shown in Fig. 2a, the endothermic peak at 247 °C indicates the transition from the orthorhombic to the

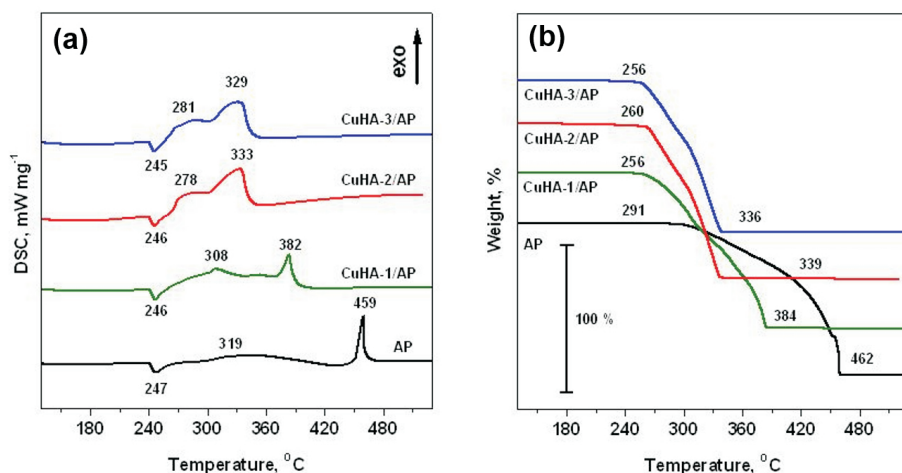


Fig. 2. (a) DSC and (b) TG scans of indicated samples

cubic polymorph [1]. The exothermic peak at 319 °C (low-temperature decomposition reaction, LTD) is due to AP incomplete decomposition to NH_3 and HClO_4 , while the second exothermic event at 459 °C (high-temperature decomposition, HTD) indicates the complete breakdown of AP [1]. As can be seen, the addition of CuHA has no practical effect on the endothermic peak of AP, whereas it significantly promotes the LTD and HTD processes. According to Fig. 2a, the temperatures of both stages decrease significantly with increasing CuHA loading. Eventually, the addition of 3 wt.% CuHA to AP leads to exothermic peaks for LTD and HTD at 281 °C and 329 °C, respectively. Of note is the fact that for CuHA-2/AP and CuHA-3/AP the stagnation decomposition (SD) stage between LTD and HTD peaks is lacking. Furthermore, CuHA also results in an increased heat release. Compared with $1020 \pm 65 \text{ J g}^{-1}$ of neat AP, the exothermic value jumps to $2150 \pm 110 \text{ J g}^{-1}$ for CuHA-3/AP. TG data, displayed in Fig. 2b, confirms the DSC results. The advancement of the LTD decomposition stage in the presence of CuHA is demonstrated by the decrease of the onset temperature of AP combustion from 291 °C to ~ 260 °C. In addition, a continuous reduction of the ending temperature of the HTD stage can be seen. A significant downshift with 78 °C is observed for CuHA-1/AP and increases further for higher mass fractions of CuHA.

On the basis of above outcomes, a three-step mechanism of the thermal decomposition of AP in the presence of CuHA can be proposed. The schematic illustration of the process is presented in Fig. 3. Firstly, decomposition of CuHA to form CuO occurs up to 250 °C (see Fig. 1d). As stated by the electron transfer theory [1], electron transfer from perchlorate ion to ammonium ion begins at 260 °C, accelerated by the partially filled 3d orbitals of Cu^{2+} on the surface of CuO through the second step. Cupric oxide is a p-type semiconductor with a

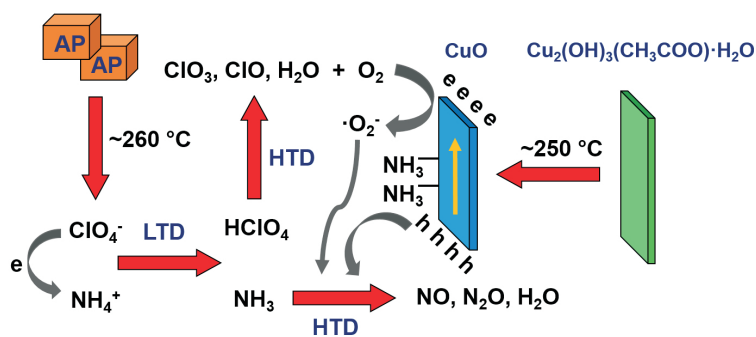


Fig. 3. Schematic illustration for the proposed reaction mechanism of AP with CuHA

band gap of approximately 1.2 eV and the conduction band electrons (e^-) and valence band holes (h^+) could be generated on its surface upon excitement with heat. Thus, during the third step, the as-produced e^- react with HClO_4 , creating superoxide radical O_2^- . The generated O_2^- and h^+ additionally react with NH_3 to form small molecules such as H_2O , NO and N_2O .

Conclusions. In summary, experimental evidences are provided that 2D copper hydroxide acetate plates can be regarded as novel highly efficient burning rate additive for AP thermal decomposition. The as-prepared 2D structures can lower the decomposition temperature of AP by 118 °C, while increasing the heat release by 91%. It was also found that the in situ generated CuO at 250 °C is an important factor to drive the catalytic process of AP combustion. These results may open new routes toward the application of lamellar organic-inorganic materials as additives in the thermal degradation of AP.

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