RESEARCH PAPER

Thermal Decomposition of Ammonium Perchlorate in the Presence of Functionalized MWCNTs

Hassan Tavakoli

Department of Physics and Chemistry, Faculty of Basic Sciences, Imam Ali University, Tehran, Iran

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ABSTRACT

In this study, functionalized multi-walled carbon nanotubes (MWCNT-COOH) were used as a nanocatalyst for thermal decomposition of ammonium perchlorate (AP) as an integral part of composite solid propellants (CSPs). Modification of MWCNTs was performed via acid treatment with concentrated aqueous solution of nitric acid, i.e. 7 M. FE-SEM and FT-IR analyses clearly revealed that nitric acid-treated materials under reflux conditions suffered the highest degree of modification and putting carboxylic acid functional groups on the top or even surface. Raman spectra displayed three types of defects in MWCNTs, i.e. D-band: sp^3-hybridization of carbons, G-band: sp^2-hybridization of carbons and D'-band: impurity on the surface. A composite was prepared by AP and MWCNT-COOH (3% wt.) via solvent-anti-solvent method and catalytic effects of these multi-walled carbon nanotubes were studied on the thermal decomposition behavior of AP by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Results showed that MWCNT-COOH lowered high temperature decomposition by 89°C and this reaction occurred in one step which was complete decomposition.

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INTRODUCTION

Chemical propellants in common are used for delivering specific impulse values ranging from about 175 up to about 300 s [1, 2]. High values of specific impulse are obtained from high exhaust-gas temperature, and from exhaust gas having very low molecular weight. To be efficient, a propellant should have a large heat of combustion to yield high temperatures, and should produce combustion products containing simple, light molecules embodying such elements as hydrogen, carbon, oxygen, and the lighter metals (aluminum, beryllium, lithium) [1-3]. There are two types of chemical propellants, solid and liquid chemical propellants [1, 2]. Two general types of solid propellants are in use [1, 2, 4, 5]. The first, the so called double-base propellant, consists of nitrocellulose and nitroglycerine, plus additives in small quantity. The other one is the composite. Separate fuel and oxidized chemicals are used, intimately mixed in the solid grain. The oxidizer is usually ammonium nitrate (AN), ammonium chlorate (AC) or ammonium perchlorate (AP), and often comprises as much as four-fifths or more of the whole propellant mix. The fuels used are hydrocarbons, such as asphaltic-type compounds, or plastics [1-5].

Ammonium perchlorate is the most common oxidant and high energy ingredient in composite solid propellants (CSPs) which occupies a

* *Corresponding Author Email: h.tavakoli@modares.ac.ir*

large proportion in the formula [6]. Thermal decomposition of this oxidant could directly affect combustive behavior (burning velocity and energy features) of solid propellant. An extensive study on the thermal decomposition of AP was carried out by researchers [7-10]. By reducing particle size of ammonium perchlorate, it could be improved, but this method is restricted because superfine AP is very dangerous [7, 8, 11]. Recently, many researchers have also investigated different catalysts on thermal decomposition of ammonium perchlorate to improve its combustive behavior [12-14]. Results showed that a small amount of catalyst could reduce temperature of thermal decomposition, especially higher pyrolytic temperature, and increase apparent decomposition heat. It could improve burning velocity and efficiency of propellant [15].

Multi-walled carbon nanotubes (MWCNTs) are nanostructures derived from rolled graphene planes [16, 17]. MWCNTs of various morphologies could be obtained depending on their preparation method [18]. Multi-walled carbon nanotubes could be used as ideal building blocks in nanotechnology. Extraordinary properties have been attributed to MWCNTs, so that a plethora of diverse technological applications ranging from wiring in integrated circuits and nanoscale components to composite materials with improved functional characteristics [19-25]. MWCNTs could be used in CSPs as catalysts or catalyst supports, where metal particles with catalytic activity may decorate along the external walls or be filled in the interior of MWCNTs [26-28].

MWCNTs are known to be agglomerated materials that will bundle together and entangle causing many defects in various applications [29]. Functionalization of this allotrope of carbon is one of several ways utilized to improve the compatibility of MWCNT and host materials. Many functional groups could be attached to MWCNT surface ranged from small molecules, such as fluorine [30], amine [31, 32], hydroxyl [32, 33], carboxyl [34-36], oxy radicals [37] and sulfonated 4-chlorophenyl [38, 39], to macromolecules like alkyl chains (butyl lithium) [40-45] that could be used in different applications, especially in the composite solid propellants. Numerous methods such as oleum method or acid treatment [34], Fischer esterification [36], Grignard synthesis [40], Friedel–Crafts reaction [46] and temperature-controlled fluorination reactor [30] have been

reported for chemical functionalization of carbon nanotubes, either on the tips or sidewall of MWCNTs [33]. It increases the ability of dispersion for MWCNT and interfacial adhesion between carbon nanotubes and nanoparticles [14, 47-51]. A supplementary and supporting method for heightening combustive behavior of AP is to use functionalized MWCNTs [51].

Here, it was tried to modify multi-walled carbon nanotubes (MWCNTs) via acid treatment and catalytic effects of MWCNTs on AP thermal decomposition as an integral part of composite solid propellants were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Characterization of functionalized MWCNTs was also completely described.

MATERIALS AND METHODS

Multi-walled carbon nanotubes (MWCNTs) with purity of 90-95% (National Iranian Oil Company, Tehran, Iran) were purchased. Average diameter and lengths of these nanotubes varied from 10 to 20 nm and from 5 to 15 µm, respectively. MWCNTs were purified before functionalization and making a composite with ammonium perchlorate (AP). They were calcined at 350°C for 2 h to remove amorphous carbon. In order to attach chemical functional groups, i.e. carboxylic acid, on the tops of nanotubes, 1 g of calcinated MWCNTs was dispersed in 100 mL of 7 M HNO_3 aqueous solution with ultra-sonication for 15 min. Then, this suspension was refluxed at 120°C for 10 h with stirring. After that, the mixture was rinsed with deionized water until that was neutral. Finally, the functionalized multi–walled carbon nanotubes (MWCNT-COOH) were separated and dried at 60°C in an oven. These MWCNT-COOH were analyzed by field emission-scanning electron microscopy (FE-SEM, MIRA3, TESCAN), transmission electron microscopy (TEM, Zeiss), Fourier transform-infrared spectroscopy (FT-IR, Nicolet Magna IR 550), Raman spectroscopy, UV-Vis spectroscopy (GBC model Cintra 101), X-ray diffraction (XRD, Philips-X'PertPro, Cu K_α, λ=1.5406 nm), thermal gravimetric analysis (TGA, STA 503, Bähr) and differential scanning calorimetry (DSC, F3 404, Netzsch).

To make a composite with ammonium perchlorate (AP), there are several methods, i.e. physical and chemical methods. In this work, a chemical method called solvent-anti-solvent

method was utilized [52]. This method avoids MWCNT-COOH from agglomeration. 518 mg of AP was first dissolved in 10 mL of distilled water and 16 mg of functionalized MWCNTs was dispersed in 10 mL of methyl isobutyl ketone followed by sonication for 10 min at room temperature. Then, these two solutions were mixed and heated at 80°C. It caused to prepare a composite with 3% wt. of MWCNT-COOH as nanocatalysts. After heating, ammonium perchlorate was homogeneously precipitated on MWCNT-COOH. Finally, the composite was tested by SEM, TGA and DSC.

RESULTS AND DISCUSSION

In order to improve the combustive behavior of ammonium perchlorate (AP) as an important oxidizer in composite solid propellants (CSPs), this oxidizer was mixed with a nanocatalyst via solvent-anti-solvent method. In this method, multi-walled carbon nanotubes (MWCNTs) functionalized by acid treatment, i.e. carboxyl functional groups, were utilized which give excellent properties to this oxidizer. It should be stated that the concentration of MWCNT-COOH in the solid mixture was 3% wt. First, functionalized MWCNTs were characterized by several analyses such as FT-IR, Raman, XRD, UV-vis, FE-SEM and TEM. Fig. 1 shows FT-IR spectra of pristine and modified multi-walled carbon nanotubes. Significant differences were observed at 1730.77 cm^{-1} (v_a C=O, carboxylic), 1128.76

cm^{-1} (v_a C-O), 1621.79 cm^{-1} (v_a C=C) which were emerged in FT-IR spectra of MWCNT-COOH. It should also be noted that the peak of v_a O-H at 3437.77 cm^{-1} was intensified which means the correct acid treatment and functionalization of MWCNTs [32, 34, 35, 53, 54]. There were carboxyl functional groups on the top or even surface of MWCNTs, which would mean that MWCNTs were well dispersed in the solution [22].

Raman spectroscopy is a powerful tool for investigation of the extent of disorder in functionalized MWCNTs. Fig. 2 represents Raman spectra of pristine and modified MWCNTs. The peak at 1357.59 cm^{-1} was attributed to D-band which means defects in disorder-induced modes or sp^3-hybridized carbons. These defects were due to finite or nanoscale graphitic planes and other forms of carbon, such as rings around defects on nanotube walls, vacancies, heptagon–pentagon pairs, kinks and heteroatoms [55]. There was another peak at 1592.86 cm^{-1} which was usually attributed to G-band or in-plan vibrations of graphite wall or sp^2-hybridized carbons [55]. These peaks were observed in both pristine and modified multi-walled carbon nanotubes. Another peak at 1626.32 cm^{-1} was observed for MWCNT-COOH which was related to D´-band due to existence of impurity on the surface. It could be easily seen for modified MWCNTs while that was not distinguishable for pristine MWCNTs [55].
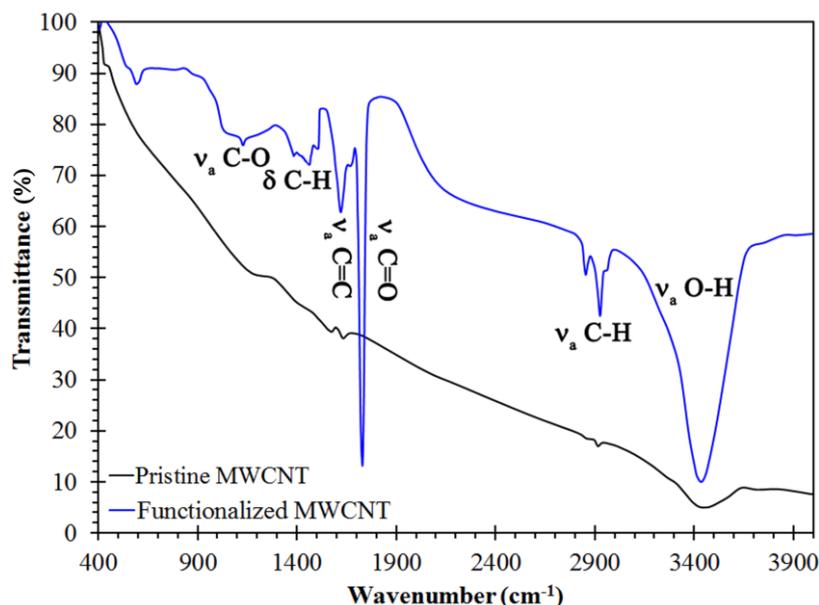

Fig. 1. FT-IR spectra of pristine and functionalized multi-walled carbon nanotubes (MWCNT-COOH).
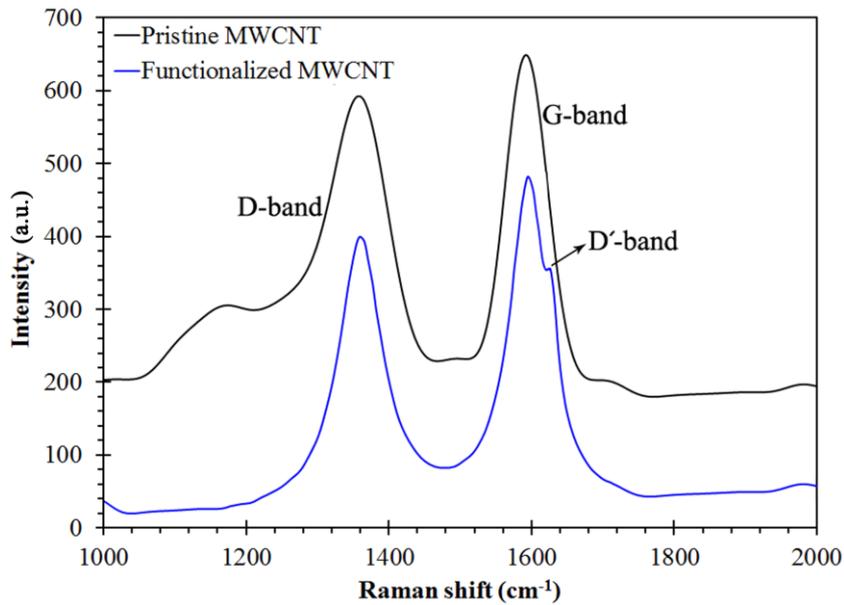
Fig. 2. Raman spectra of pristine and functionalized multi-walled carbon nanotubes (MWCNT-COOH).

It should be stated that D-band to G-band (I_D/I_G) area ratio indicates that functionalization affects surface structure of MWCNTs. I_D/I_G area ratios of pristine MWCNTs and acid-treated MWCNTs are 0.84 and 0.91, respectively, which revealed that functionalized MWCNTs were properly synthesized in this research [46].

Fig. 3 shows X-ray diffraction patterns (XRD) of pristine and functionalized MWCNTs.

Significant diffraction pattern of pristine MWCNTs was appeared at 26.02° [35]. This peak was corresponded to (002) reflection plane or also known as interlayered spacing between adjacent graphite layers. (002) reflection peak was observed at the same value in modified MWCNTs diffraction. Interestingly, the intensity of diffraction peak at (002) in acid treatment of MWCNTs decreased. This was an indication of loose carbon nanotube flosses
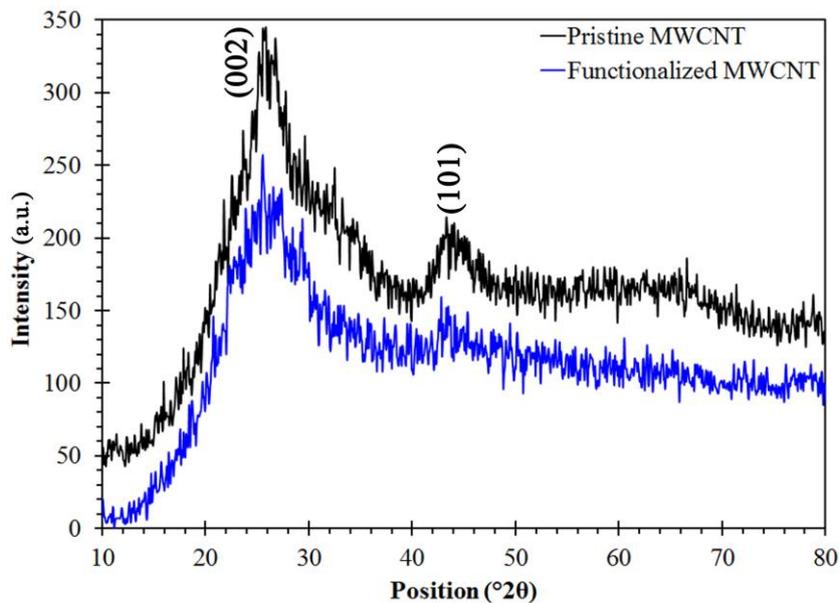

Fig. 3. XRD patterns of pristine and functionalized multi-walled carbon nanotubes (MWCNT-COOH).
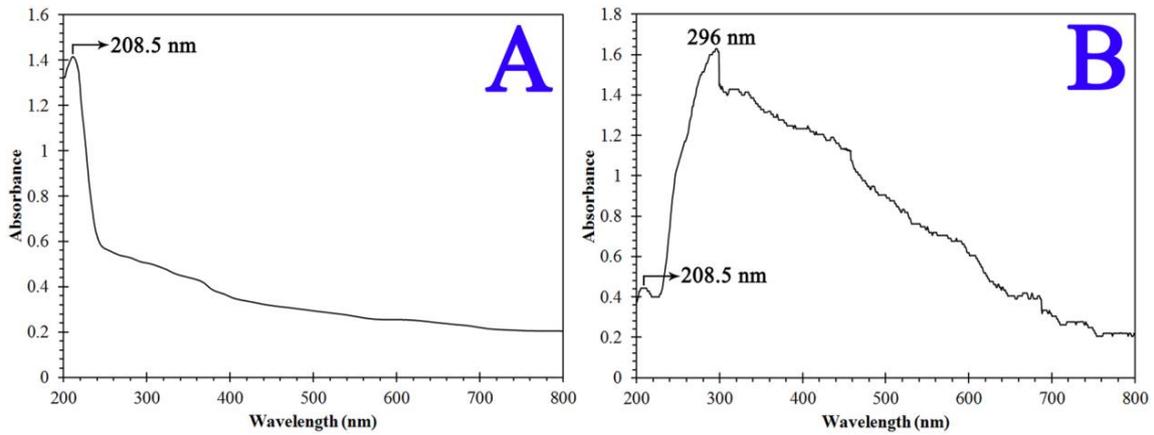
Fig. 4. UV-Vis spectra of A: pristine and B: functionalized multi-walled carbon nanotubes (MWCNT-COOH).

after treatment which they form less ordered in the functionalized ones. Furthermore, there was another peak at 43.82° which was related to (101) reflection plane. From XRD patterns, it could be concluded that functionalized MWCNTs still had same cylindrical wall and inter-planar spacing

after functionalization process. Thus, the structure of MWCNTs was protected even after undergoing the treatment.

Fig. 4 depicts UV–Vis spectra of pristine and functionalized MWCNTs via acid treatment. Both spectra had a maximum absorbance around 208.5
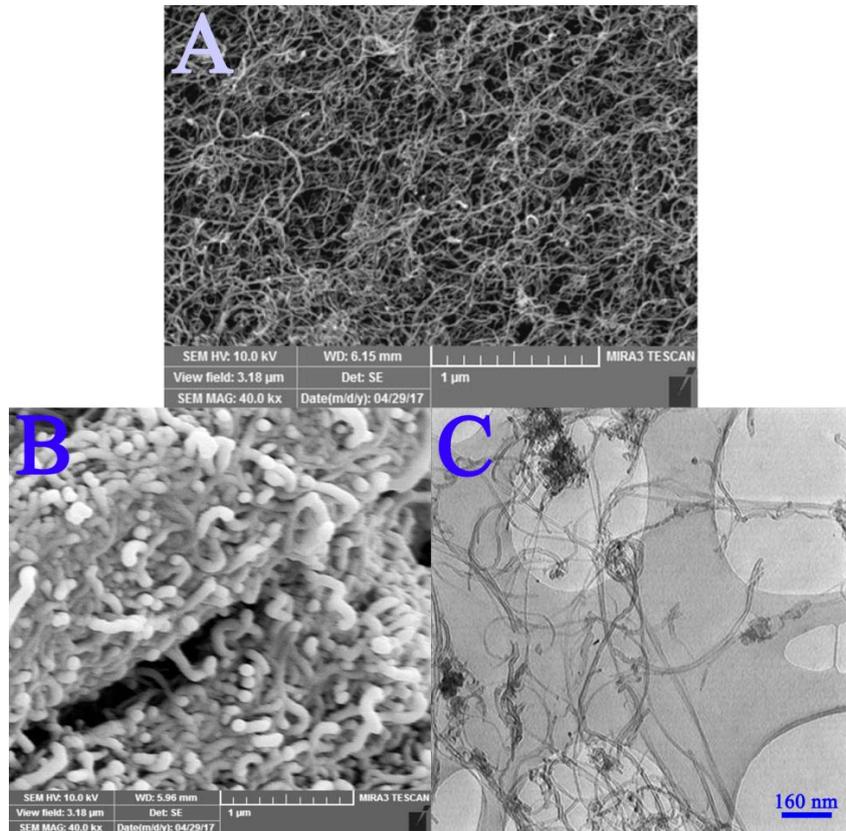

Fig. 5. A: FE-SEM image of pristine MWCNTs, B: FE-SEM and C: TEM images of functionalized multi-walled carbon nanotubes (MWCNT-COOH).
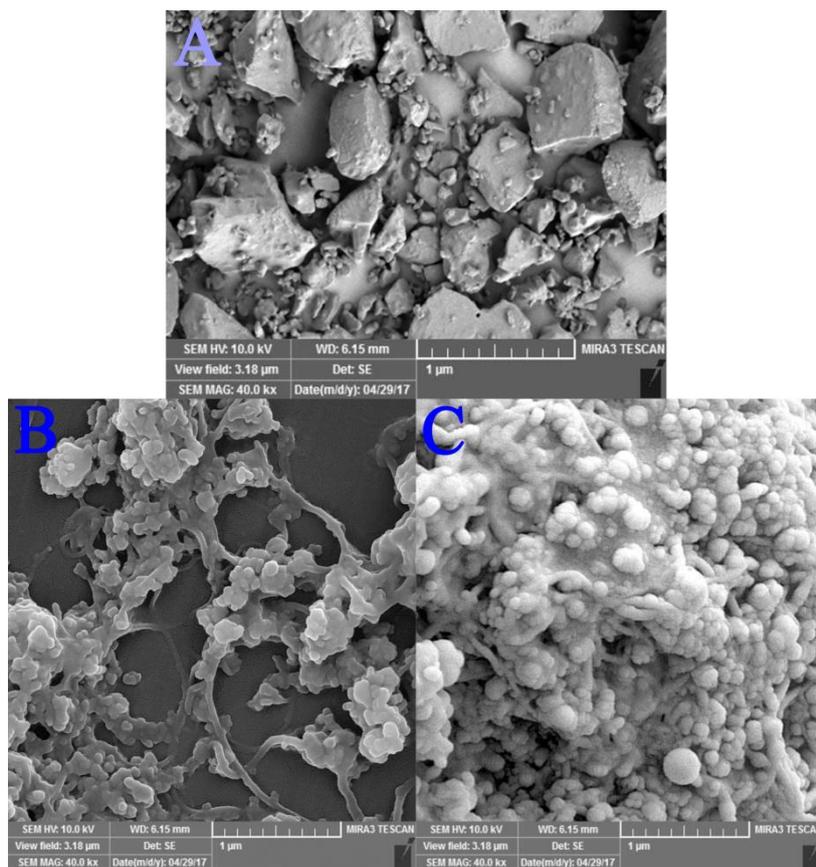
Fig. 6. FE-SEM images of A: ammonium perchlorate (AP) and its composite with B: pristine and
C: functionalized multi-walled carbon nanotubes.

nm which was related to p–p* charge transition of C–C aromatic bond of CNT structure [34]. While on the contrary, there was another peak at 296 nm as C=O bond for modified MWCNTs which meant carboxyl and hydroxyl functional groups on the surface of CNTs were formed (Fig. 4B). Based on literature, the first peak was narrow related to pristine MWCNTs which indicated agglomeration of carbon nanotubes (Fig. 4A) [34]. Briefly, these results proved the presence of functional groups on the surface of MWCNTs and led to improve the performance of thermal decomposition for ammonium perchlorate.

FE-SEM and TEM images of functionalized multi-walled carbon nanotubes (MWCNT-COOH) are presented in Figs. 5B and C. FE-SEM image of MWCNTs was also illustrated in Fig. 5A. Cylindrical structures of modified MWCNTs could be clearly seen with 20 to 30 nm in diameter and 5 to 10 μm in length. In order to study the thermal decomposition of ammonium perchlorate (AP) in

the presence of MWCNT-COOH as nanocatalyst, a composite was made with them and FE-SEM image of this product is displayed in Fig. 6C. These materials were homogenously mixed with each other which could be analyzed as composite. FE-SEM images of initial AP and AP/ MWCNTs composite are shown in Figs. 6A and 6B, respectively.

Fig. 7 exhibits TGA and DSC curves of pure AP, pristine MWCNTs, functionalized MWCNTs and their composites with 3% wt. of catalysts at rate of 10°C/min. The endothermic peak at 244.1°C for pure ammonium perchlorate was due to crystallographic transition from orthorhombic to cubic form (Fig. 7A). This transition remained unaltered after addition of pristine or functionalized MWCNTs (Figs. 7D and 7E). The first low temperature exothermic peak (LTD) at 289.6°C was observed for AP which was attributed to its partial decomposition and producing intermediates (NH_3 and $HClO_4$). Ammonium perchlorate underwent

complete decomposition at the second and main high temperature exothermic (HTD) at 443.6°C which intermediate products were converted into volatile products (O_2, Cl_2, N_2O, NO_2, HNO_3, H_2O, HCl, ClO and HOCl). After addition of pristine MWCNTs or MWCNT-COOH (3% wt.), noticeable changes were experienced at high temperature decomposition (HTD) of AP. Compared to pure AP, HTD shifted from 443.6°C to 389.6°C and 354.6°C

for pristine MWCNTs and MWCNT-COOH at rate of 10°C/min, respectively (Figs. 7A, 7D and 7E). This drastic decrease in temperature by 54°C and 89°C indicated an efficient catalytic effect on the thermal decomposition of ammonium perchlorate. This decrease was significant in functionalized MWCNTs, i.e. from 562.5°C to 354.6°C (207.9°C), which was due to the synergistic action of this binary composite (AP/3% wt. MWCNT-COOH)
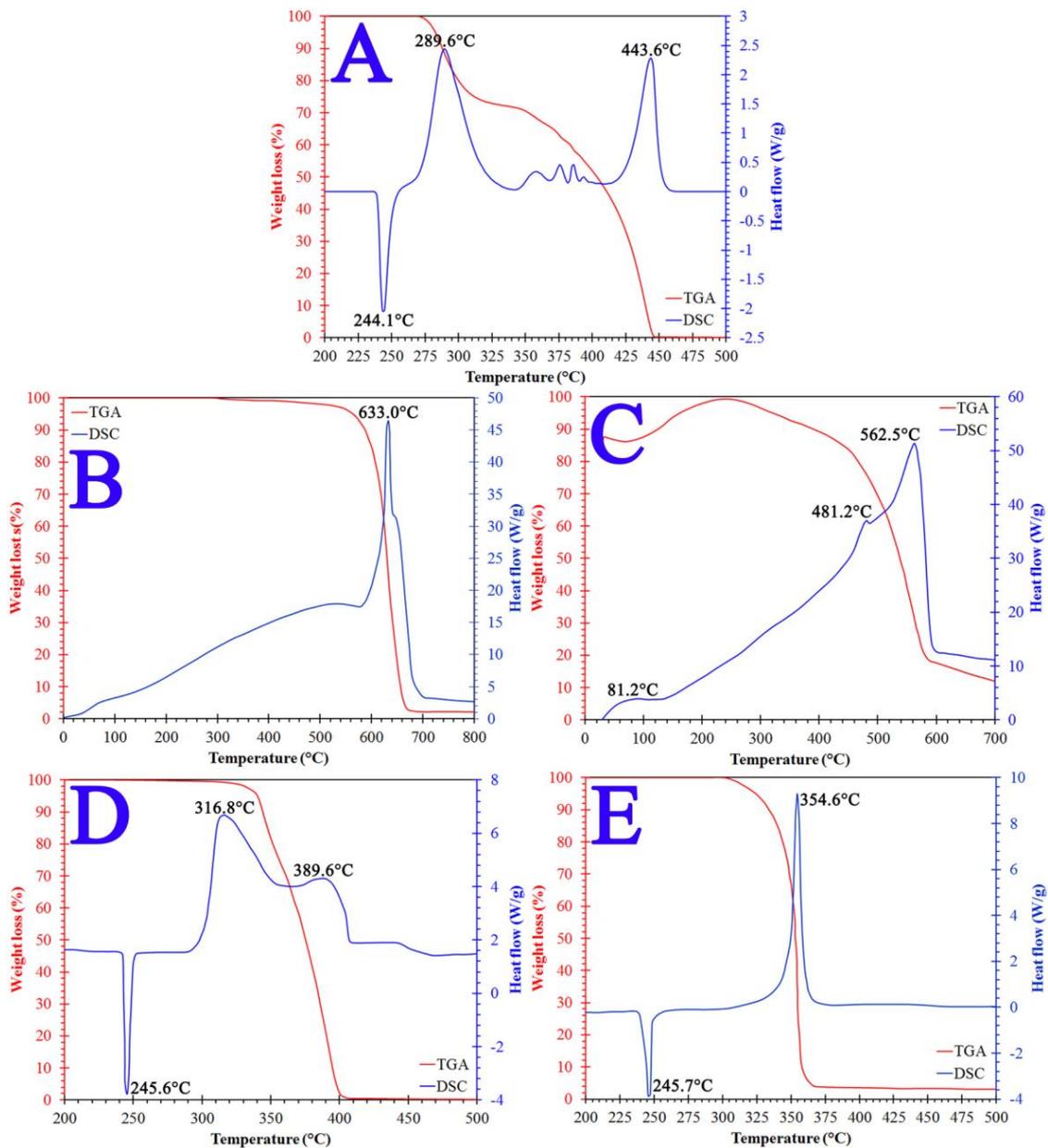

Fig. 7. TGA and DSC curves of A: AP, B: pristine MWCNTs, C: functionalized multi-walled carbon nanotubes (MWCNT-COOH) D: AP/MWCNTs, and E: AP/MWCNT-COOH composite at rate of 10°C/min.

causing an enhancement in the catalytic activity (Figs. 7C and 7E). Such a marked reduction in HTD was also attributed to the presence of a large number of active sites, higher surface area and smaller particle size of modified MWCNTs [52]. Another interesting observation was a high heat release (ΔH) of 1308.71 J/g (AP/3% wt. MWCNT-COOH) compared to 388.86 J/g for pure AP which was the highest value achieved so far by using MWCNT-COOH as a nanocatalyst.

As it was observed in TGA curves, thermal decomposition of pure ammonium perchlorate showed a two-step weight loss (Fig. 7A). At low temperature (317.0°C), in which weight loss was 28.4%, it could be related to partial decomposition of AP and formation of intermediates, i.e. NH_3 and $HClO_4$ by dissociation and sublimation, respectively. At high temperature (450.6°C), in which weight loss was 71.8%, it could be related to complete decomposition of intermediate volatile products. In the presence of functionalized MWCNTs nanocatalyst, TGA curves showed that weight loss was a one-step process which meant a complete decomposition of ammonium perchlorate (Fig. 7C). Gaseous species, such as NH_3 and $HClO_4$, were absorbed on the MWCNT-COOH surface. This catalyzed the reaction towards completion affecting the high-temperature decomposition peak. The reaction scheme proposed for the LTD was dominated by the proton transfer mechanism with the formation of NH_3 and $HClO_4$. The proton was trapped by either ClO_3^- or by ClO_4^- whose protonated forms decomposed readily to form ClO_2, a strong oxidizer. ClO_2 oxidized NH_3 and NH_4^+ to form the observed decomposition products dominated by N_2O. The reaction scheme proposed for the HTD was initiated by the sublimation of AP and subsequent decomposition of the sublimated AP on the MWCNT-COOH to form NH_3 and $HClO_4$ which reacted further to form the observed products dominated by NO_2.

CONCLUSION

Ammonium perchlorate (AP) is an important material for preparation of composite solid propellants (CSPs) and its performance affects combustive behavior of propellants. In this research, multi-walled carbon nanotubes (MWCNTs) were modified by acid treatment and used as nanocatalysts. They were made a composite with AP via solvent-anti-solvent method. Several analyses such as FT-IR, Raman, XRD and UV-Vis

spectra confirmed functionalization of MWCNTs. FT-IR and UV-Vis spectra revealed carboxylic acid functional groups on the top and even surface of MWCNT-COOH. Raman spectra showed defects on the surface which was due to acid treatment. XRD patterns exhibited characteristic peak of MWCNT which existed in the modified form. Based on FE-SEM and TEM images, diameter and length of MWCNT-COOH were 20-30 nm and 5-10 µm, respectively. FE-SEM image of composite displayed functionalized multi-walled carbon nanotubes were homogenously combined with ammonium perchlorate. TGA and DSC analyses of pure AP, MWCNT-COOH and their composite with 3% wt. of MWCNT-COOH disclosed excellent catalytic performance on thermal decomposition of AP. When modified MWCNTs were added, the peak of high-temperature decomposition decreased by 89°C and heat released (ΔH) during decomposition was 1308.7 J/g, compared to 388.86 J/g for pure AP. TGA analysis showed one-step thermal decomposition of ammonium perchlorate which was because of catalytic behavior of functionalized MWCNTs (MWCNT-COOH).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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