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# Graphene Titanium dioxide nanocomposite (GTNC): One Pot Green Synthesis and Its Application in Solid Rocket Propellant

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A green process was developed for graphene-titanium dioxide nano-composite (GTNC) synthesis by dispersing titanium dioxide nanoparticles ($TiO_2$) and graphene nano-sheet (GNS) in ethanol via ultrasonication followed by microwave irradiation. The synthesized GTNC were well characterized by various tools viz. XRD, HRTEM, FTIR and Raman spectroscopy. Also, Simultaneous Thermal Analysis (STA) and Differencial Scanning Calorimetry (DSC) techniques have been employed to study the enhancement of catalytic activity of GTNC for decomposition of Ammonium perchlroate (AP). The GTNC with 5 wt % in AP was found to be highly effective catalyst for AP decomposition. The decomposition temperature decreases from 412.87 °C to 372.50 °C and ΔH increases from 2053 to 3903 J/g. Further, such GTNC was identified as a effective burn rate enhancer (i.e. combustion catalyst) for AP based composite propellant for solid rocket propellant as confirmed by STA, DSC, activation energy calculations and burn rate measurements. The results show that burn rate of propellant increases by 24% for $TiO_2$ nanoparticles based composition compare to base composition, whereas a significant increase of 50% is achieved in the presence of GTNC. Hence, the performance is improve significantly to solid rocket propellant.

## Introduction

Since their work of Nobel laurates Geim and Novoselov, many attempts have been made by different researchers in order to dig out useful properties out of graphene[1]. Graphene has a panorama to attract attention due to its unique properties like high carrier mobility, room temperature quantum effect and ambipolar electric field effect[2]. Drastic reduction of such distinctive properties of graphene is possible with increase in number of graphene layers until it reaches to 3D form[3,4] i.e**.** graphite which is a bulk form of graphene with multilayered structure. Graphene with ten or fewer such graphitic layers reveal distinct properties in comparison to the bulk form[5]. These special properties makes graphene one of the most appealing material for its applications in various areas such as composite, electronic and advance mechanical resonator[6,7]. Graphene has an exclusive ability of increasing the catalytic activity by placing the suitable metal oxide/ metal nanoparticles on its surface. As a result, the number of effective catalytic site on graphene surface increases. In nanotechnology, graphene also has utility being used as a substrate.

Although, Graphene has many applications, presently, graphene aerogel has been used as energetic material in solid rocket propellant[8]. Thus, we decided to explore the use of graphene and graphene based metal/metal oxide for as burn rate enhancer as well as a combustion catalyst to decompose ammonium perchlorate (AP), a well known oxidizer for composite propellant[9]. AP is the major source of energy in space vehicle and missiles. The rate of decomposition and heat release of AP can be enhanced by addition of different burn rate modifier like ferric oxide ($Fe_2O_3$), copper oxide (CuO), and copper chromite (CuO, $Cr_2O_3$), nickel oxide (NIO), etc[10-14]. According to reported literature[15], $TiO_2$ works as a catalyst for AP decomposition reaction. To increases the efficiency of titanium dioxide further, researchers have reduced the particle size to nanometers. For titanium dioxide nanoparticles, higher catalytic activity has been observed due to enhancement of the surface to volume ratio. Concurrently, the viscosity of the propellant mix. also increases abruptly which was undesirable. Thus, it would be interesting to obsereve the effect of a nano-composite comprising of $TiO_2$ and graphene i.e. GTNC on the burn rate of propellants.

In the present article, we have demonstrated the simple preparation method of GTNC and its application as combustion catalyst for AP decomposition and burn rate enhancers of composite propellant. The application of GTNC in propellant

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Electronic Supplementary Information (ESI) available: [[details of raw materials, instrumentation, nano $TiO_2$ synthesis, Raman spectra, additional FESEM images, additional HRTEM images, Detail procedure for thermoelectric properties measurement, Summary of thermoelectric properties of the best composite of inorganic and organic materials.]. See DOI: 10.1039/b000000x

compositions was studied using differential scanning calorimetry (DSC), Simultaneous Thermal Analysis (STA) and Thermogravimetric analysis (TGA). The structure, composition and morphology of the as-prepared GTNC have been characterized by Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Field Emmission Scanning Electron Microscope (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), and X-ray diffraction (XRD).

## Experimental details

### General

Graphitic flakes (Reinste nano ventures, India), ethanol (absolute, AR, Merck), graphite powder, $H_2SO_4$, $NaNO_3$, NaOH, $H_2O_2$ (30%), $K_3Fe(CN)_6$, $KMnO_4$, myristic acid and $TiCl_4$ were purchased from Sigma-Aldrich (USA). All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in Milli-Q water (18 MΩ $cm^{-1}$ ). myristic acid (absolute, AR, Merck), titanium tetrachloride (absolute, AR, Merck), were used without further purification. Sonication was conducted by using ultrasonication bath (35 kHz, Kudos). Microwave irradiation was carried out by a microwave reactor (make :Raga). FESEM was carried out with Quanta 200, FEI. High resolution transmission microscopic (HRTEM images) characterization was carried out by TACHNAI F-30, FEI with 300 kV field emission gun(FEG). Nano $TiO_2$, graphene and GTNC were dispersed in methanol with ultrasonication. The dispersion was placed on TEM grid. Solvent was evaporated by oven drying. Fourier Transform Infrared Spectroscopy (FTIR) were collected by Nicolet 5700, (make: Thermoscientific). Raman traces were measured by Invia refelex micro raman, Renishaw. X-Ray Defraction traces were collected by X- Ray Defractometer D8 advance, Bruker with Cu Kα source at measurement angle range 2θ=2-90° with a scan rate 2°/ min. Differential Scanning Calorimetry (DSC) curves were collected by DSC-7, Perkin Elmer. Thermo gavimetric analysis (TGA) was performed by Metter Toledo, Model-TGA/SDTA851.

### Synthesis and Characterization

### *Synthesis*

*a)Synthesis of anatase $TiO_2$ nano-particles*

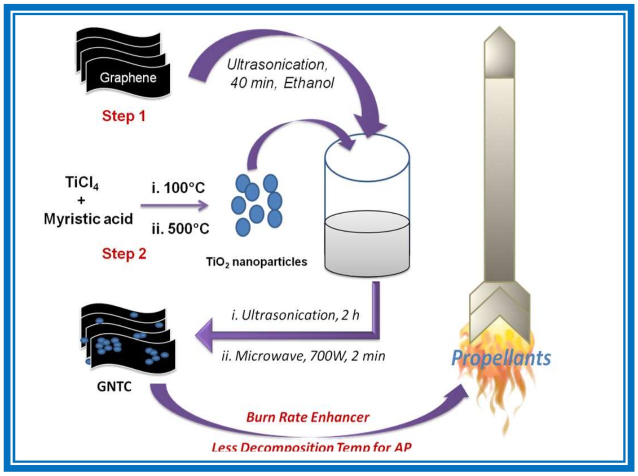
Anatase-$TiO_2$ nanoparticles have been synthesized by using myristic acid and titanium tetrachloride ($TiCl_4$). The detailed synthesis method for $TiO_2$ nanoparticles is based on the literature method published by Khanna et al.[16] where obtained $TiO_2$ powder was calcined at 500 °C to increase its crystalline anatase-$TiO_2$ ( see also S1 in ESI).

*b) Synthesis of graphene from graphite flake*

The graphene was prepared in three steps as reported in the literature[14, 40]. In the first step, graphite oxide was prepared from graphitic flakes by Hummers method. In the second step, thermally expanded graphene oxide (TEGO) was prepared by thermal expansion/ exfoliation at 1050°C (Ar, 30 s). Finally, graphene nanosheet (GNS) was obtained by hydrogen reduction of TEGO at 400 °C for 2 hours.

*c) Prepration of Graphene/$TiO_2$ nano-comppsite* (GTNC)

GNTC was prepared by dispersing 50 mg graphene nanosheet in ethanol through ultasonication and by adding pre-dispersed titanium dioxide nanoparticles to the graphene dispersion. The so-developed dispered mixture was further ultrasonicated for 2 hrs followed by drying at ambient condition to remove solvent. After drying, GTNC was deposited on a petridish and subjected to microwave irridiation for 2 min to have better exfoliation. The overall process of synthesis of GTNC is depicted in **Scheme 1**.



**Scheme 1:** Schamatic representation of synthesis and application of graphene-titanium dioxide nano-composite (GTNC)

### *Charecterization of GTNC*

X-Ray diffraction scan were recorded for the samples to comfirm the presence of anatase $TiO_2$ nanoparticles and graphene in the GTNC (See **Figure 1a**). The $TiO_2$ nanoparticles synthesized by sol-gel method showed slightly crystalline nature with $2\theta$ peaks lying at 25.25 (101), 37.8 (004), 47.9 (200), 53.59 (105) and 62.36 (204). The broad peak at $2\theta$ = 25.8 ° in the GTNC indicates a random packingof graphene sheets and corresponds to (002) plane of graphite. The FT-IR spectrum of the GTNC did not reveal any information regarding the presence of organics in the product. However, it was confirmed that pure graphene is present in the sample as peaks for graphene oxide were absent (see **Figure 1b)**.

The Raman Spectroscopy was used to anaslyse the quality of graphene sheet before and after nanocomposite formation by above mentioned techniques. **Figure1(c)** represents the Raman traces of graphene, nano $TiO_2$ and GTNC

The most pronounced Raman traces are D band at 1310 $cm^{-1}$ corresponds to defect and G band 1575 $cm^{-1}$ corresponds to in plane vibration of $sp^2$ carbon. 2D band at 2727.4 $cm^{-1}$ which is generated due to a two phonon double resonance process has also been observed. The lower intensity D band indicates the presence of a small amount of defects on graphene flakes. The I(D)/I(G) of the graphene-titanium dioxide composite increased by 1.5 times (0.7) with respect to pure graphene (0.497). Several defects with $sp^2$ domain were formed during nanocomposite preparation. **Figure 1(c)** and **(d)** shows characteristic Raman signatures of composites.

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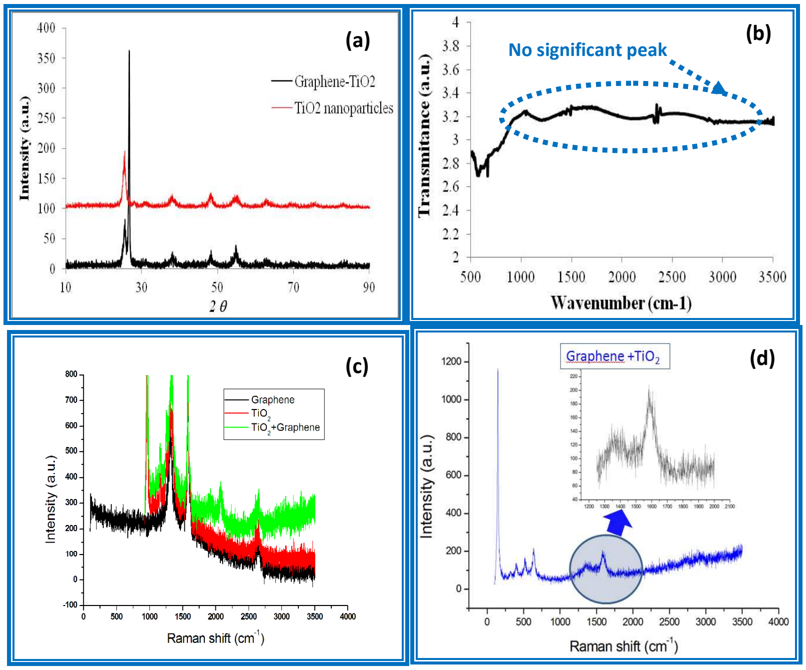


**Figure 1:** (a) XRD profiles of $TiO_2$ nanoparticles and graphene-titanium dioxide nano-composite(GTNC) and (b) FTIR spectrum of graphene –titanium dioxide (GTNC) nano-composite (c) Raman traces of graphene, $TiO_2$ and GTNC (d) Raman traces of GTNC

High resolution transmission electron microscopy (HRTEM) of the GTNC were used to inspect the presence of $TiO_2$ nanoparticles in graphene (See **Figure 2 a,b**). The results confirmed the size of $TiO_2$ nanoparticles and graphene in the nanometer regime where the observed size of the $TiO_2$ nanoparticles was below 20 nm. Thin graphene layers were clearly visible in the images which acted as a substrate for $TiO_2$ nanoparticles. Additional HR-TEM images of graphene alone are provided in the electronic supporting information (ESI: **Figure S2**). Similarly, Field emmission scanning electron microscopy (FESEM) images (**Figure 2 c,d**) depicts uniform dispersion of $TiO_2$ nanoparticles over graphene layers. It was cleary observed that $TiO_2$ nanoparticles are present in aggregated form in the GTNC. The exfoliated structure of graphene layers along with nano-sized spherical shaped of $TiO_2$ will ensure enormous availibilty of the surface of the GTNC nano-composite. The high surface area of GTNC an be vital for its catalytic behaviour.

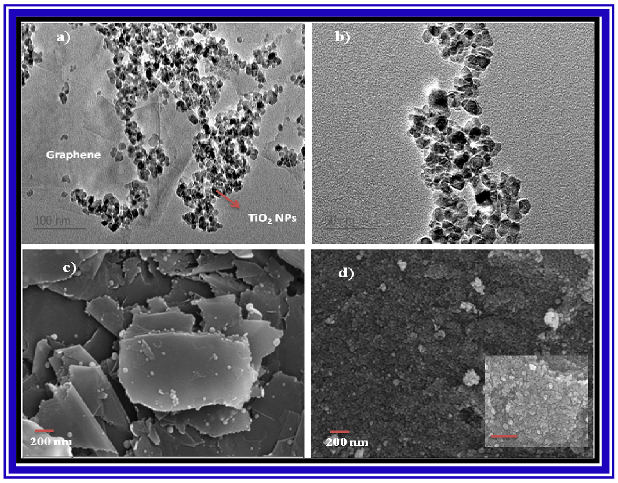


**Figure 2:** HR-TEM images of  (a) graphene-titanium dioxide nano-composite (GTNC) and b) $TiO_2$ nanoparticles. FE-SEM images (c) graphene -titanium dioxide nano-composite (GTNC) and d) $TiO_2$ nanoparticles. The images reveal that the spherical shaped $TiO_2$ nanoparticles are nicely dispersed in the layers of graphene.

### ❖Formulations evaluation of AP decomposition

A total of three formulations containing 1-5 wt. % graphene, GTNC and $TiO_2$ nanoparticles along with AP have been made by simple mixing with mortor and pastle. After proper mixing, each formulation was subjected to thermal analysis for studying the decomposition behavior of AP in presence of catalyst.

## Composite propellant

### ❖*Raw materials and formulation*

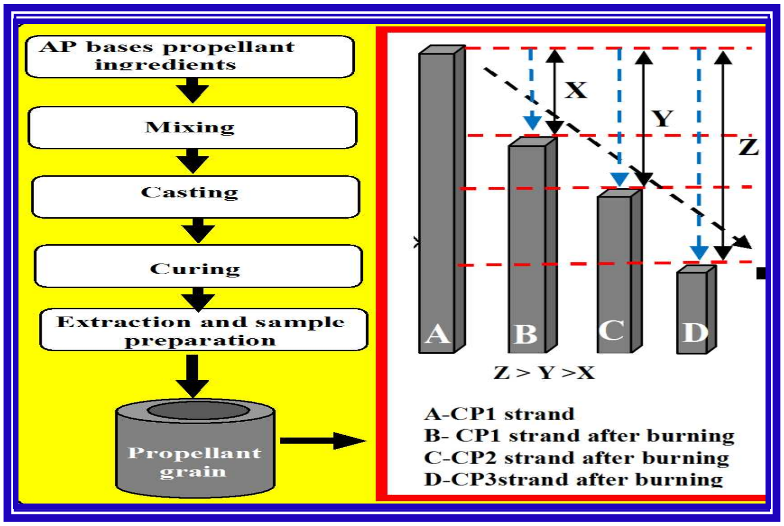
To evaluate the burn rate enhancing capability of GTNC with respect to known burn rate enhancer for composite propellant, three seperate formulations have been processed. Composite propellant consists of two parts, i.e. binder and solid ingredient. The binder, consisting of hydroxy terminated polybutadiene, (HTPB: OH value 40-50 mg/g, moisture 0.15%, from Orion Chemicals), was cured with toluene di-isocyanate (TDI: purity 99%, RI 1.565-1.567 at 30 °C; from Bayers, India). Dioctyl adipate (DOA: saponification value 303 ±3, moisture 0.5%, from Subhas Chemicals) was used as a plasticizer to increase the processibility. Indigenously made GTNC, titanium dioxide nanoparticles, graphene were used as enhancer burning rate. The  1:2 mixture of trimethylolpropane (OH value 1220, moisture 0.5%, :purchased from Celenese) and butane-1,4-diol (OH value 1220, RI 1.444 ±0.002 at 30 °C, moisture 0.5%, purchased from BIAF, India) was used as an adduct in the composition. We have used two different sizes of ammonium perchlorate in the propellant formulations. The first one is research grade ammonium perchlorate  (purity 99%, density 1.95, from Tamilnadu chlorates, India) with an average particle size of 300 µm. The second one was made by grinding ammonium perchlorate (> 99% pure) in a fluid energy mill to an average particle size of 50 µm. Aluminum metal powder (from MEPCO, India) of average particle size 15 µm, was used as a metal fuel. The propellent formulation coded as CP-1 did not contain any burn rate modifier i.e. GTNC or $TiO_2$ nanoparticles. Whereas, CP-2 contained 1 part (over the batch) of $TiO_2$ nanoparticles alone as modifiers and CP-3 consisted of 1 part (over the batch) of GTNC alone as modifier.  The details of ingradients of propellant formulation are presented in **Table 1.**

**Table 1: Propellant formulation**

| Sr. No | Ingredients | CP-(wt.%) | CP-2 (wt.%) | CP-3 (wt.%) |
|---|---|---|---|---|
| 1. | Hydroxyl terminated polybutadiene  (HTPB) | 10.06 | 10.06 | 10.06 |
| 2. | Dioctyl Adipate (DOA) | 3.0 | 3.0 | 3.0 |
| 3. | Adduct: n-butane diol: Tri methylol propane (2:1) | 0.12 | 0.12 | 0.12 |
| 4. | Toluene diisocuane (TDI) | 0.72 | 0.72 | 0.72 |
| 5. | Ammonium perchlorate (AP), 300µ) | 52.5 | 52.5 | 52.5 |
| 6. | Ammonium perchlorate (AP), 50µ) | 15.6 | 15.6 | 15.6 |
| 7. | Aluminum (Al) | 18.0 | 18.0 | 18.0 |
| 8. | Graphene-$TiO_2$ nano-composite | 0.0 | 0.0 | 1.0 part over the batch |
| 9. | $TiO_2$ nanoparticles | 0.0 | 1.0 parts over the batch | 0.0 |

### *Propellant processing flowchart*

AP based composite propellant has been made by following **Scheme 2**. Before going for processing, raw material characterization is one of the important step. As isocyanate curing is moisture sensitive, hence moisture content of the ingredients should be below 0.05%. Otherwise, it forms voids in the propellant. After weighing, ingredients were tranferred in to verticle planatory mixer. Mixing was carried out by following a predefined mixing cycle with proper addition sequence. To get a better quality of the mix., vacuum was applied. After mixing, casting was carried out by vacuum casting method. This casted propellant was cured at 50-60°. After curing, propellant strands were prepared and subjected to the test.



**Scheme 2:** Schamatic representation of propellant processing and variation of propellant strend after burning

***Propellant characterization***

Initially, we calculated some of the important ballistic properties like characteristic velocity (C*), flame temperature ($T_f$) and specific impulse ($I_{sp}$) using NASA CEC-71 software. Several important properties have been evaluated during the course of propellant processing in order to study the effect of GTNC in AP based composite propellant. Since, viscosity is one of the important parameters; viscosity of the propellant mix was characterized by Brookfield viscometer (T-type, HBT model) at a 40°C. These measurements were carried out at one hour interval up to 4-5 hrs during processing. The strand burning rate of the propellants was determined in the pressure range 5-9 MPa by employing an acoustic emission technique after completion of curing reaction[20,21]. This process involved the combustion of the strand which was ignited by means of a nichrome wire in the nitrogen pressurized steel bomb. The generation of acoustic signal and calculating the burn rates for each sample by the methodology adopted in our previous report[14]. Mettler density kit has been used for the determination of the densities of propellant compositions (density 1.432 g/cc, heat of formation -565.8 kJ/mol) where toluene was used as a liquid. The sensitivity to impact stimuli of the propellant compositions was determined with a fall hammer apparatus (2 kg drop weight) using the Bruceton Staircase method [22] and the results were given in terms of the statically obtained 50% probability of explosion (H50). The friction sensitivity was measured with a Julius Peter apparatus by incrementally increasing the load from 0.2 to 36 kg, until there was an ignition/explosion in five consecutive test samples.

The prepared sample was heated homogeneously at a constant rate (5 °C/min) in a Woods metal bath, until it exploded or ignited at the ignition temperature. The ignition temperature was measured by Julius Peters apparatus. Thermal analysis of the propellants was carried out by STA (Q-600,USA), Perkin Elmer Pyris Diamond DSC apparatus at a heating rate of 20 °C/min under an $N_2$ atmosphere (sample mass ~10 mg). The mechanical properties were obtained with an Instron device (Model TIC-1185, UK). The operating instrumental parameters were always maintained constant; gauge length 25 mm, crosshead speed 50 mm/min. The stress and strain properties were determined using a dumbbell-shaped specimen as per specification ASTM-D-638.

## Results and Discussion

***Catalytic effect on AP decomposition***

Three steps were involved in AP decomposition. In the 1st step endothermic phase transition i.e. orthorhombic to cubic occurs at 242 °C. An exothermic process was observed at 304°C, named as low temperature decomposition (LTD) of AP corresponds to the intermediate formation like $NH_3$ and $HClO_4$ by dissociation and sublimation**.** The high temperure decomposition started on AP surface at 360 °C and continued to completion at ~450 °C (detail mechanism is given in **Figure 3a**). To study the efficiency of catalytic behavior of GTNC for AP decomposition, three different compositions with different catalysts like graphene, nano titanium dioxide and GTNC with 1-5 wt. % were made and characterized by means of DSC and STA. **Figure 3** shows comparative bar chart of peak temperature **(Figure 3b),** final temperature of TGA analysis **(Figure 3c)** and ΔH of ammonium perchlorate(AP) **(Figure 3d)** in presence of 1-5 wt.% of graphene, graphene-$TiO_2$ and $TiO_2$ nanoparticles [see also **Figure S3**]. DSC traces like ΔH increased and decomposition temperature decreased with increase in GTNC concentration. Decrease in decomposition temperature and increase in ΔH value indicates efficient catalytic behaviour of GTNC for AP decomposition. In TGA, final deccomposition temperature was found to decrease with increase of GTNC concentration [1-5 wt.%].

Numerous mechanisms have been proposed for thermal decomposition of AP[23-28] whereas, two of them attracted the attention of researchers and they are still debatable. Majority are electron transfer and proton transfer mechanisms which we have well described in our previous work[14] The present experimental findings suggest that that GTNC accelerates both LTD and HTD

(**Figure 3a**). In the simultaneous process of gas and solid phase reactions of LTD, dissociation as well as sublimation takes place.[30, 31] The controlling step for LTD is transfer of electron from $ClO_4^-$ to $NH_4^+$ whereas transformation from oxygen ($O_2$) to superoxide ($O_2^-$) should be the controlling step for HTD. Since graphene exhibits several unique properties like good conductivity, distinct electric field effect with a charge concentration as high as $10^{13}$ $cm^{-3}$ and mobility[32] as high as $1.5 \times 10^4$ $cm^2V^{-1}s^{-1}$, the movement of elentron in graphene is much faster than that of metal atoms.Therefore, it is possible attain an effective speed which is 300 times less compared to speed of light in a vacuum and travel large distance with out any deflection.[33] In this way, the synthesized GTNC may accelerate the electrons to speed up the above mentioned controlling steps. Then, $HClO_4$ generates $O_2$ which subsequently form superoxide ($O_2^-$) more rapidly and decomposes $NH_3$ which results complete decomposition of AP.

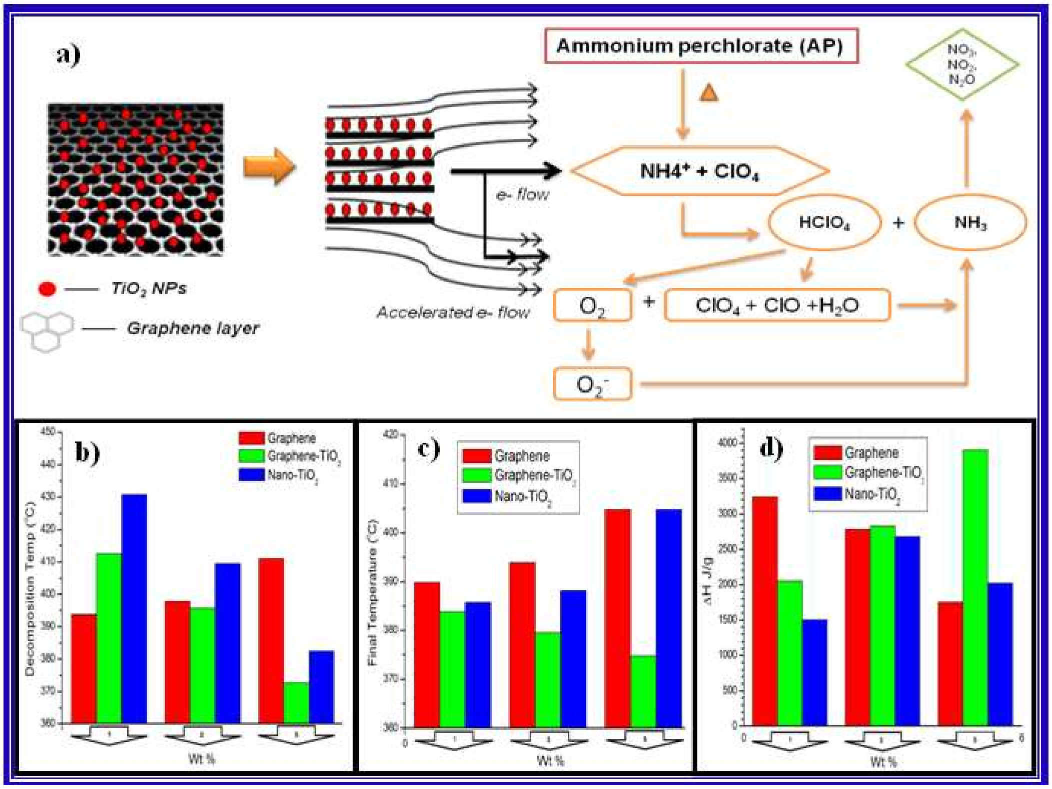
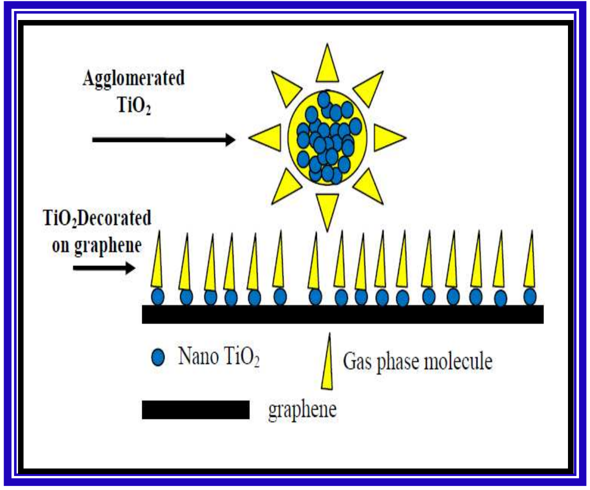


**Figure 3:** a) Decomposition mechanism of AP in presence of GTNC, b) Comparative bar diagram of decomposition temoperature, **c)** Comparative bar diagram of TGA final temperature and d) ΔH with different filler concentration (1, 3, and 5 wt.%).

As bare Titanium oxide nanoparticles does not posses any supporting substrate, it is more likely to form aggregates and rendering less active sites to adsorb $NH_3$ and $HClO_4$ in order to accelerate the reaction. However, when decorated on graphene, which is the best catalyst substrate with the theoretical surface area of 2600 $m^2/g$ [34], the decorated nanoparticles are able to unfold on the graphene substrate to genertate more active sites and react with $NH_3$ and $HClO_4$, which accelerates the catalysis process. However, it should be noted that a significant difference was observed for the catalytic performance of 3% and 5% GTNC. In addition to the AP decomposition reaction, we have studied propellant burn rate enhancing ability of GTNC. The enhancement was found to be much higher when compared to the base composition i.e. CP-1 and nano $TiO_2$ based composition i.e. CP-2 etc. During combustion of propellant, AP decomposes along with combustion of propellant binder (HTPB, DOA, curative etc.) at a faster rate due to rapid electron flow from graphene substrate to the combustion step which results higher burn rate of propellant (see **Table S4, S5, S6**). Thermal decomposition of AP by proton transfer mechanism has been proposed by Jackobs et al. [35, 36, 37] and the same has been discussed in previous studies in detail[14]. According to this mechanism, perchloric acid gets desorbed more rapidly than ammonia[36, 37] which causes incomplete oxidation of ammonia and results saturated atmosphere of ammonia.[36, 37] HTD decelerates and undergoes incomplete transformation. During HTD, de-acceleration and incomplete transformation takes place producing NO, $O_2$, $Cl_2$ ,and $H_2O$ products in gas phase reaction. As a result of LTD, accumulation of reaction product and formation of new active centres took place which consequents decomposition of the orthorhombic modification. Kaidymov and Gavazova[38, 39] formulated that the process takes place at the surface of the crystal due to adsorption and desorption of ammonia and chloric acid. The addition of dopent changes the concentration of the protons in the activity of the orthorhombic modification with respect to perchloric acid decomposition is an important stage through which thermal decomposition proceeds and quite high compared to the cubic modification. The following **Scheme-3** represents that nano $TiO_2$ exists in agglomer form, hence effective surface area for catalytic lattice at the time of decomposition. It suggest that the catalytic activity is less. By employing graphene, $TiO_2$ nanoparticle has been decorated over the graphene substrate and intact its nano form. Hence, effective surface area increases abruptly, which reflets by its high catalytic activity to dards AP decomposition. **Figure 4** represents the DSC traces of AP and AP with different fillers.



**Scheme 3:** Decomposition of propellant in presence of GTNC

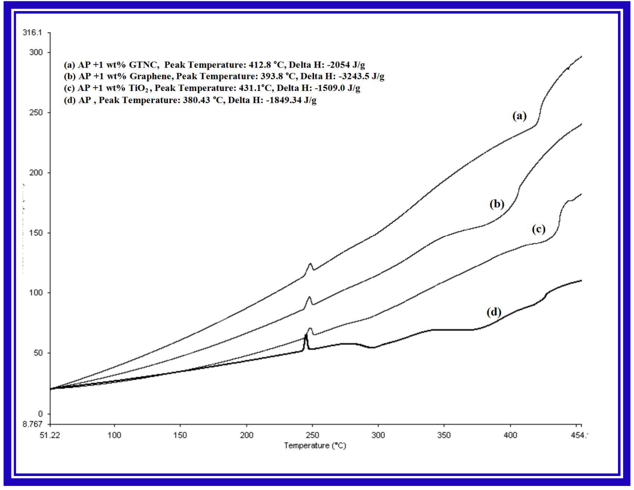


**Figure 4:** DSC curves of AP and AP with different fillers (1 wt. %)

Further, the effect of GTNC as burn rate enhancer for composite propellant has been studied. DSC, DTA-TGA, density, viscosity, calorimetric value (cal-val), sensitivity and mechanical properties were used to evaluate these propellant formulations. The detail assignments have been given in Table 2,3 and S5, S6 in ESI). The decrease in properties like peak temperature (**Table 2**), activation energy (**Table 2**) and final temperature of DTA (**Table 2**) were observed and this decrease is drastic for GTNC (CP-3). The final temperature obtained from TGA was relatively less affected for CP-3 compare to CP-2 (**Table 2**). The GTNC based composition shows more stability compare to $TiO_2$ based composition. Since, the stability is directly proportional to the propellant safety, it would be one of the important parameters for the propellant field. According to **Table 3**, viscosity of the propellant mix decreases by addition of GTNC whereas propellant composition containing nano $TiO_2$ shows high viscosity which is detrimental to the propellant processing. Mechanical properties of the cured propellant (see **Table 3**) increases drastically as compared to the $TiO_2$ based (CP-2) and control composition (CP-1). During burn rate measurement, it revealed that burn rate increases with pressure ( from 5-10 MPa). From base composition to $TiO_2$ nanoparticles, burn rate increases about at each pressure. But in case of GTNC, burn rate inctreases trumendously (50 %) at each pressure. The above experimentation only shows that GTNC is very effective decomposition catalyst as well as effective burn rate enhancers for composite propellant. GTNC is first time reported as AP decomposoition catalyst as well as burn rate enhancers (see **Figure.5**) for AP based composite propellant.

**Table 2. Thermal analysis results with different burn rate enhancer in propellant composition**

| Sr. No | Composition | DSC | | | DTA @ 20°C/min | | | TGA@ 20°C/min | |
|---|---|---|---|---|---|---|---|---|---|
| | | Peak temp. (°C) @ 10°C /min | ΔH (J/g) | Act. Energy (KJ/M) | initial temp. (T initial, °C) | Max. temp. (Tmax, °C) | Final temp ( Tmax, °C) | Temp. (°C) | weight loss (%) |
| 1. | CP-1 | 403.5 | -1680.3 | 260.4 | 242.4 | 298.4 | 375.4 | 249.5-420.4 | 65.4 |
| 2. | CP-2 (nano TiO2) | 375.2 | -1635.2 | 210.4 | 242.5 | 308.2 | 359.2 | 249.8-392.5 | 66.8 |
| 3. | CP-3 (Gr-TiO2) | 368.2 | -1630.4 | 196.2 | 242.8 | 307.3 | 354.4 | 249.2-410.2 | 68.2 |

**Table 3. Physico-chemical properties with different burn rate enhancer in propellant composition**

| Sr. No | Comp$^n$ | Viscosity (poise) Initial at 40°C | Mechanical properties | | |
|---|---|---|---|---|---|
| | | | UTS, kgf/cm$^2$ | % elongation | E-Modulus, kgf/cm$^2$ |
| 1. | CP-1 | 7000-8000 | 5.5 | 40.0 | 34.0 |
| 2. | CP-2 (nano $TiO_2$) | 10000-12000 | 6.2 | 44.5 | 36.4 |
| 3. | CP-3 (Gr-$TiO_2$) | 4000-5000 | 8.28 | 52 | 54 |

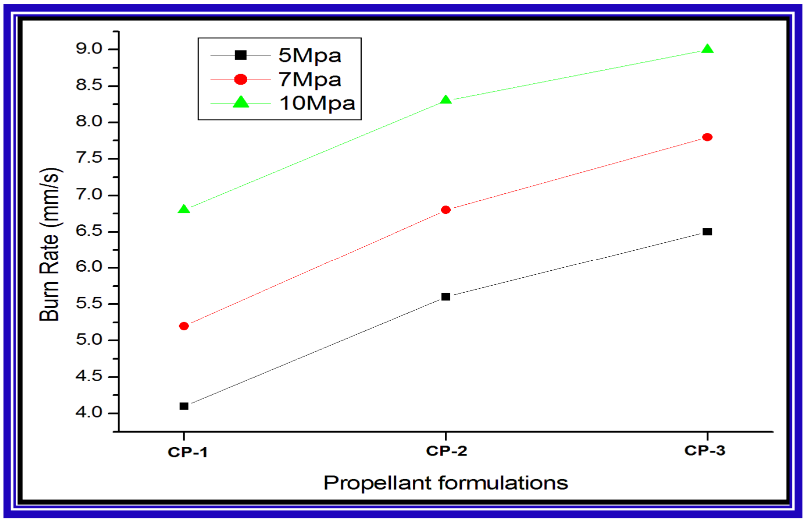


**Figure 5:** Variation of burn rate with pressure for different propellant composition

## Conclusions

In the present article, we have synthesized Graphene-Titanium dioxide nano-composite (GTNC) by dispersing titanium dioxide ($TiO_2$) nanoparticles and graphene nano-sheets (GNS) in ethanol via ultrasonication followed by microwave irradiation.This methodology is not only cheap but also ecofriendly. Further, we have explored GTNC as catalyst for AP decomposition as well as burn rate enhancers of propellants for solid rocket propellant. Simultaneous Thermal Analysis (STA) and Differencial Scanning Calorimetry (DSC) techniques revealed the enhancement of catalytic activity of GTNC for decomposition of Ammonium perchlroate (AP). The GTNC with 5 wt % in AP was found to be highly effective as decomposition temperature decreased 412.9 °C to 372.5 °C and ΔH increased from 2053 to 3903 J/g. Additionally, such GTNC nano-composite performed as a effective burn rate enhancer for propellents. The results show that burn rate of propellant increases by 24% for $TiO_2$ nanoparticles based composition, whereas a significant increase of 50% is achieved in the presence of GTNC. Interestingly, the effective titanium dioxide concentration in GTNC is about 50% less as compared to that of pure $TiO_2$ nanoparticles. Therefore, the designed GTNC was found to be an excellent burn rate modifier for advance AP based propellant which is useful for solid rocket propellant system. Besides this, processing of propellant turn to be very easy due to decrease in mix. viscosity and also mechanical properties are enhanced significantly in presence of GTNC.

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