Application of NiO synthesized through large scale synthesis in propellants as ballistic modifier

P.Vijayadarshan^{a,b,1}, J.Venkata Viswanath^{a,b,1}, T.Mohan^{a,b}, Amarnath Gupta^b, T. V. Chowdary^b, A. Venkataraman^{a,c}*

^aMaterials Chemistry laboratory, Department of Materials Science, Gulbarga University, Kalaburagi-585106, Karnataka. India.

^bR and D center, Premier Explosives Limited, P.O. Peddakandukur-508286, YadadriDistrict, Telangana, India.

^cDepartment of Chemistry, Gulbarga University, Kalaburagi-585106, Karnataka. India.

*Corresponding author Email: raman.dms@gmail.com

Abstract:

Present study in an emphasis of employing Nickel oxide (NiO) synthesized via large scale synthesis throughself-propagating low temperature combustion reaction as a burn rate modifier in composite solid propellant (CSP). Vielle's law is employed to study the burn rate of the formulated CSP. The results obtained from the synthesized NiO are compared with the reported commercial Fe_2O_3 and CUCRO. The results infer that the NiO is one among the potential candidates to be employed as a burn rate modifier in CSP.

Keyword: Nickel oxide nanoparticle, Composite solid propellant, ballistic modifier, Vielle's law, Crawford bomb strand burner.

1. Introduction:

NiO is synthesized and employed in various chemical reactions as a battery cathode, gas sensor, electrochromic films, magnetic material, dye sensitized photocathodes [1], electronic devices,

including catalyst since past 2 decades. Its applicability as a burn rate modifier is also well known [2]. Various routes of synthesis to produce NiO are briefly given below.

Dharmaraj et al. 2006 have synthesized NiO nanoparticles using nickel acetate and poly (vinyl acetate) precursor [3]. BahariMollaMahaleh et al. 2008 have adopted chemical precipitation synthesize NiO nanoparticles and reported the effect of surfactant method to (Polyvinylpyrolidone, polyethylene glycol and acetyl trimethyl ammonium bromide) on particle size distribution [4]. Shah 2008 has synthesized NiO nanostructures without organic addition [5]. Fasaki et al. 2010 have reported the structural, electrical and mechanical properties of NiO thin films grown by pulsed laser deposition [6]. Manohar A. Bhosle and Bhalchandra M. Bhanage 2015 have synthesized NiOnanorods through microwave assisted decomposition of nickel acetate and reported the catalytic behavior of thus synthesized NiOnanorods in synthesizing benzimidazole, benzoxazole and benzothiozole [7]. Rahdar et al. 2015 have synthesized NiO nanoparticles by co-precipitating nickel chloride hexahydrate and sodium hydroxide [8]. Jeevanandam and Ranga Rao Pulimi 2012 have reported the nanocrystalline NiOsynthesized through sol-gel method and homogeneous precipitation method [9]. Lay Gaik Teoh and Kun-Dar Li 2012 have synthesized NiO nanoparticles through surfactant (nonionic copolymer F108) mediated sol-gel method [10].Nurul Nadia MohdZorkipliet al. 2016 have synthesized NiO adopting sol-gel method using isopropanol and polyethylene glycol [11].El-Kemaryet al. have synthesized NiOnanoparticles employing thermal decomposition of nickel hydroxide nanoparticles and applied as glucose sensor. Muhammad Imran Din and Aneela Rani 2016 have synthesized NiO nanoparticles through green synthesis from plant extracts, microbial extracts and naturally occurring biomolecules and reported the antimicrobial property of thus synthesized NiO nanoparticles [12].

Researchers have synthesized NiO in nano scale with different physical forms which includes nanoparticles, nanorings, nanosheets, nanoribbons and hollow nanospheres and applied them for different purposes depending on their needs. All the reports to date describe about small scale synthesis ofNiO nanostructures. Recently Vijayadarshan et al. 2017 have communicated the large scale synthesis and characterization of NiO nanoparticles employing low temperature self-combustion route [13].

Metal oxides synthesized through low temperature self-combustion reaction possess uniform particle size, high surface areas and the reported SEM images shows the uniform morphology of the particles [14-18]. Thus synthesized metal oxides are employed in preparing polymer nanocomposites and the results of characterizations show homogenous distribution of particles throughout the polymer matrix [19-22]. This peculiar behavior encouraged us to use the large scale synthesized NiO nanoparticles via low temperature self-combustion reaction in formulating CSP where HTPB is a polymer used to maintain homogeneity of the propellant. Metal oxide nanoparticles are known for their catalytic activity as burn rate modifiers in the formulation of CSP. Iron oxide (Fe₂O₃)[23], copper chromite (CUCRO) [24], titanium oxide(TiO₂) [25]etc. are the metal oxides which are being widely used by industries to formulate CSPs. NiO nanoparticles are also used as burn rate modifier in double base propellantformulations. The burn rate results of formulated CSP are higher to that of burn rate obtained for CSP without metal oxides.

2. Materials and methods:

NiO nanoparticles synthesized via low temperature self-combustion reaction [13] are employed to formulate CSP. The formulation of CSP with NiO involves homogeneous mixing of $9.5\pm2\%$ HTPB (Energetic Binder), $18\pm2\%$ of Aluminium (fuel), $69\pm2\%$ of Ammonium Perchlorate (Oxidizer) (AP), $1.0\pm0.5\%$ of NiO (Ballistic modifier). The composition is mixed with Butanediol (BDO) as a linking agent of the binder, dioctyladipate (DOA) as a plasticizer, toluene di-isocyanate (TDI) as a curing agent and lecithin is a processability improver in formulating CSP. The mixture is mixed well for homogeneity in a sigma mixer [23-24]. Trimodel addition (addition of coarse, fine and ultrafine) of AP is adopted which assisted in achieving compactness and consolidation to the CSP. The same CSP composition with commercial Fe₂O₃ is prepared and used for comparison. Cured CSP is cut into strands of $6.0\times6.0\times120.0$ mm to test burn rate using Crawford bomb strand burner. The CSP is further cut into dumbbell shape with 4.0 mm thickness and 6.0 mm widthto perform mechanical testing of CSP. The sample preparation for all the tests carried out as per American Society for Testing and Materials International (ASTM) standards [26]. Formulation of CSP along with burn rate tests andmechanical property tests are carried out at Premier Explosives Limited, Hyderabad, India.

3. Results and Discussion:

The NiO added CSP is tested for burn rate under a pressure range of 4.90 – 8.83 MPa at room temperature. The results are shown in the form of pressure vs burn rate graphs drawn employing Vielle's law [27]. The graphs show a burn rate of 6.83 mm/sec at the initial pressure of 4.90 MPa and increased to 8.99 mm/sec at the pressure of 8.83 MPa. Whereas the burn rate for CSP without metal oxide (WOMO) is 6.82 mm/sec at the initial pressure of 4.90 MPa and increased to 8.36 mm/sec at 8.83 MPa pressure. The graph shown in figure 1 clearly infers the increased burn rate of CSP with NiO addition. The pressure exponent calculated employing Vielle's law for the CSP with NiO is 0.462 while for CSP WOMO is 0.351. Vielle's law for calculating pressure exponent is given in equation 1.



The comparative study of burn rates of CSP burn rates where CUCRO and NiO are taken as burn rate modifiers is shown in figure 2. The results describe the similar mode of increment in burn rate for CSP withNiO as that of CSP with Fe_2O_3 and CUCRO but with less burn rate.



CSP with NiO shows a tensile strength of 3.814 MPa at a maximum force of 37.4 N, which is almost 250% when compared with the value reported by Bose and Pandey 2012. The % elongation for the CSP with NiO is 11.23, which matches the results obtained by Bose and Pandey 2012. The E-modulus for the CSP with NiO is 16.27 MPa. The E-Modulus reported by Bose and Pandey 2012 with the same CSP composition with Fe_2O_3 is 3.344 MPa. The increased E-modulus of CSP with NiO when compared with that of reported CSP with Fe_2O_3 infers the high loading capacity of CSP with NiO. The shore hardness for CSP with NiO is 84. The decreased burn rate when compared to that of CSP with commercial Fe_2O_3 or CUCRO is reported for CSP with NiO. The catalytic behavior of NiO in oxidation of A1 and HTPB are given in figure 3 the graphical abstract.



4. Conclusion:

The CSP is formulated by employing NiO nanoparticles synthesized in large scale via low temperature self-combustion route as ballistic modifier. The NiOnanoparticles show agood catalytic property as burn rate modifier in CSP. Although the burn rate for CSP with NiO is lesser than CSP with Fe_2O_3 or CUCRO theimproved mechanical properties when compared to the reported have gained the attention towards employing NiO nanoparticles as burn rate modifier in CSP formulation. Transition metal oxides having higher oxidation state metals or metal ions with different oxidation states have showed even higher burn rates. Lower oxidation state and availability of single oxidation state throughout the catalyst may be the reason for such low burn rate of CSP with NiO.

References:

- El-Kemary M, NagyN, El-MehassebI. Nickel oxide nanoparticles Synthesis and spectral studies of interactions with glucose. Materials Science in semiconductor processing 2013; 166:1747-1752.
- [2] Abhijit Dey, VinitNangare, Priyesh V. More, Md Abdul Shafeeuulla Khan, Pawan K. Khanna, ArunKantiSikder, Santanu Chattopadhyay. A graphene titanium dioxide

nanocomposite(GTNC): one pot green synthesis and its applicationin a solid rocket propellant. RSC Advances 2015; 5: 63777-63785.

- [3] Dharmaraj N, Prabhu P, Nagarajan S, Kim CH, Park JH, Kim HY. Synthesis of nickel oxide nanoparticles using nickel acetate and poly (vinyl acetate) precursor. Materials Science and Engineering B 2006; 128: 111-114.
- [4] BahariMollaMahaleh Y, Sadrnezhaad SK, Hosseini D. NiO nanoparticles synthesis by chemical precipitation and effect of applied surfactant on distribution of particle size. Journal of Nanomaterials 2008; 470595. DOI: 10.1155/2008/470595
- [5] Shah MA. A versatile route for the synthesis of nickel oxide nanostructures without organics at low temperature. Nanoscale. Research Letters 2008; 3: 255-259.
- [6] Fasaki I, Koutoulaki A, Kompitsas M, Charitidis C. Structural, electrical and mechanical properties of NiO nano thin films grown by pulsed laser deposit. Applied Surface Science2010; 257: 429-433.
- [7] Manohar A. Bhosle, Bhalchandra M. Bhanage. Rapid synthesis of nickel oxide nanorods and its applications in catalysis. Advanced Powder Technology 2015; 26 (2):422-427.
- [8] Rahdar A, Aliahmad M, Azizi Y. NiO nanoparticles synthesis and characterization. Journal of nanostructures 2015; 5:145-151.
- [9] Jeevanandam P, Ranga Rao Pulimi V. Synthesis of nanocrystallineNiO by sol-gel and homogeneous precipitation method. Indian Journal of Chemistry 2012; 51A: 586-590.
- [10] Lay Gaik Teoh, Kun-Dar Li. Synthesis and characterization of NiO nanoparticles by sol-gel method. Materials Transactions2012; 53 (12): 2135-2140.
- [11] Nurul Nadia MohdZorkipli, Noor HaidaMohdKaus, Ahmad Azmin Mohamad. Synthesis of NiO nanoparticles through sol-gel method. Procedia chemistry 2016;19: 626-631.
 - [12] Muhammad Imran Din, Aneela Rani. Recent advances in the synthesis and stabilization of Nickel and Nickel oxide nanoparticles: A green adeptness. International journal of Analytical Chemistry 2016; ID 3512145:14 pages.
 - [13] Vijayadarshan P, Mohan T, VenkataViswanath J, Venugopal KJ, Srinivasa Rao NV, Amarnath Gupta, Venkataraman A. Large scale synthesis of Nickel oxide (NiO) by selfpropagated combustion reaction. Material Science Research India 2017; Communicated.

- [14] Arunkumar L, Vijayanand H, Basavaraja S, Balaji SD, Venkataraman A. Combustion Synthesis of Nanosizedγ-Fe₂O₃: StructureMorphology and Bonding.Mater. Sci. Res. Ind. 2004; 02(1); 13-16.
- [15] Basavaraja S, Vijayanand H and Venkataraman A, Deshpande U P, Shripathi T.Characterization of γ-Fe₂O₃ nanoparticles synthesized through self-propagating combustion route Syn React. Inorg. Metal. Org. Nano-Metal Chem.2007;37: 409-412.
- [16] Mahesh D. Bedre, BasavarajaS,Raghunadan Deshpande,BalajiDS,
 VenkataramanA.Preparation and characterization of cobalt oxide nanoparticles via solution
 combustion method.Nanoscience and nanotechnology an Indian journal 2009;3(1): 5-8.
- [17] Sharanabasava VG, Venugopal KJ, Ravishankar Bhat, Raghunandan Deshpande, BasavarajaS, Srinivasa RaoNV, VenkataramanA.Large scale synthesis and characterization of γ-Fe₂O₃ nanoparticles by self-propagating low temperature combustion method. Int. Journal of Science Research2012a; 01(02): 77-79.
- [18] Sharanabasava VG, Ravi Shankar Bhat, Raghunandan Deshpande and Venkataraman A., Synthesis and characterization of nickel oxide nanoparticles by self-propagating low temperature combustion method. J.Recent Research in Science and Technology 2012b;4(4):50-53.
- [19] MallikarjunNN, VenkataramanA, AminabhaviTM.A study on γ-Fe₂O₃ Loaded Poly (methyl methacrylate) Nanocomposites. J. Appl. Poly. Sci 2004 ;94:2551-2554.
- [20] VijayanandHV, ArunkumarL, GurubasawarajPM, Veeresha SharmaPM, BasavarajaS, SaleemA, VenkataramanA, Anil Ghanwat, MaldarNN.Synthesis and Characterization of Polyimide-γ-Fe₂O₃ Nanocomposite. J. Appl. Poly. Sci 2007;103: 834-840.
- [21] Mahesh D. Bedre, BasavarajaS,Raghunadan Deshpande, Balaji DS,Arunkumar L,GovindarajB, VenkataramanA. Preparation and characterization of polyaniline NiO nanocomposites via interfacial polymerization. Journal of Metallurgy and Materials Science2010;152(2): 149-154.
- [22] Hajeebaba KI, BasavarajRB, NagabhushanaH, MahaleshDevendrappa, SharanabasammaAmbalgi, BasavarajaSannakki, MathadRD. DC conductivity study of polyaniline/NiO nanocomposites prepared through green synthesis. Materials Today Proceedings 2016; 3: 3850-3854.

- [23] Bose P, Pandey KM. Desirability and assessment of mechanical strength characteristics of solid propellant for use in multi barred rocket launcher. International journal of chemical engineering and application 2012; 3 (2): 114-124.
- [24] VenkataViswanathJ, VijayadarshanP, MohanT, Srinivasa RaoNV, Amarnath Gupta,VenkataramanA. Copper chromite as ballistic modifier in a typical solid rocket propellant composition: A novel synthetic route involved. Journal of energetic materials 2017;DOI:10.1080/07370652.2017.1313911.
- [25] VesnaRodic. Effect of Titanium (IV) oxide on composite solid propellant properties. Scientific technical review 2012; 6 (3-4): 21-27.
- [26] Pandarinath Rao N, Solanke C, Bihari BK, Singh PP, Bhattacharya B. Evaluation of mechanical properties of solid propellants in rocket motors by indentation technique. Propellants, Explosives, Pyrotechnics 2016; 41 (2): 281-285.
- [27] Trache D, Maggi F, Palmucci I, DeLuca LT, Khimeche K, Fassina M, Dossi S, Colombo G. Effect of amide-based compounds on the combustion characteristics of composite solid rocket propellants. Arabian Journal of Chemistry 2015; DOI: 10.1016/j.dt.2016.05.002.

