The Effect of Nitrogen on Morphology of Bismuth Tellurite Nanostructured Thermoelectric Materials Synthesis by Rational Method

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Abstract—**Nanostructure thermoelectric materials are showing much interest due to having potential to use in future thermoelectric devices for energy harvesting applications as figure of merit of the Bismuth Telluride (Bi_2Te_3) bulk materials is not much impressive to use for such applications. Hence, various morphologies of nanostructured materials such as nanoparticles (0D) and nanowires(1D) are showing more interest due to enhancing the figure of merits. In this present work, average diameter of 10-20nm nanoparticles, and nanoparticles decorated nanowires with average diameter of 16-25nm having length of several micro-meter were prepared by rational synthesis method with nitrogen and without nitrogen protection at 140^oC. The experimental results revealed that nanoparticles were grown when N_2 was introduced as a protection gas whereas nanoparticles decorated nanowires were observed without the presence of N_2. Hence, the morphologies of the bismuth telluride are greatly affected by the different synthesis parameters and the outcome of our findings will help to understand the morphology and size effects on the properties of these thermoelectric materials for future energy harvesting applications.**

Keywords: Nanostructure; Bi_2Te_3;   Rational   synthesis; Thermoelectric Devices.

I. INTRODUCTION

Thermoelectric materials that convert electrical energy into thermal energy or vice versa have been used in cooling, refrigeration, and power generation [1]. Thermoelectric(TE) devices, which are semiconductor systems that can directly convert electricity into thermal energy for cooling or heating or recover waste heat and converting into electrical power, are increasingly in demands and having the potential to make important contributions to reducing CO2 and greenhouse gas emissions and providing cleaner forms of energy[2]. The performance of thermoelectric devices depends on the figure of merit (ZT) of the materials, given by $ZT = (\alpha^2 T/\rho\ K_T)$, Where α ,T, ρ and K_T are α is the thermoelectric power or Seebeck coefficient, of the material, ρ and K_T, electrical resistivity and the total thermal conductivity respectively ,and T is the absolute temperature   of the thermoelectric materials[3-5]. Several literatures have been reported that nanostructure thermoelectric materials such as Bi_2Te_3 nanostructures with various morphologies such as nanoparticles[7-9],nano-sheets[10],   nanowires,[11-12], hollow nano-spheres[13] improve significantly ZT >1[6]. There are several synthesis processes to obtain the

nanostructured Bi_2Te_3 materials with various morphologies by using hydrothermal method [14], bismuth telluride based nanowires including the solvothermal synthesis [15-16]. Such, hydrothermal and solvothermal process are usually required high pressure and long reaction time. Till now much progress has been reported to prepare nanostructure bismuth telluride with various sizes and shapes such as microwave assisted method [17-18],mechanical alloying [19], hot pressing [20], spark plasma sintering [21] and wet chemical method [22]. Previously, there have been only few studies showing   the   growth   of Bi_2Te_3 heterostructures   with dimensions over hundreds of nanometers using expensive precursors   and   surfactant   [23-24].   Out   of   several thermoelectric materials, bismuth telluride (Bi_2Te_3) nanostructured thermoelectric materials were considered for various applications due to the higher figure of merit value [27].   However,   more   research   efforts   still   require understanding   the   various   morphology   and   sizes nanostructured bismuth telluride (Bi_2Te_3) thermoelectric materials. Here, we report the effect of nitrogen as protection gas during the rational synthesis method of synthesis Bi_2Te_3 nanomaterials. In this paper, various morphologies control by the synthesis process parameter to obtain nanoparticles and nanoparticles decorated nanowires having different sizes of bismuth telluride (Bi_2Te_3) are discussed.

II. SYNTHESIS METHOD

All the chemicals used in the present synthesis were analytical grad were all purchased from sigma Aldrich (USA). In a typically synthesized by a two-step solution phase reaction in which grow spherical shape of Bi_2Te_3 nanoparticles and then perform a diffusion reaction to diffuse Bi into Te nanoparticles. First of all, for the synthesis of Bi_2Te_3 nanoparticles, 20ml of ethylene glycol (EG) was added to a three neck flask followed by adding of 0.2g of polyvinyl pyrrolidone (PVPmw-40000) 0.6g of NaOH and 3 mmol of TeO_2 powder (99.999%). Nitrogen was purged through the system to keep the reaction in an oxygen-free environment the mixture was stirred and heated to 140ºC with nitrogen protection and then 0.6 ml of hydrazine hydrate solution was injected into the reaction. It was observed that the yellow-transparent solution started to turn into black slurry, hydrazine hydrate was added to the above solution as a reducing agent, which was kept under 140ºC for 1 hour after Te form completely. A bismuth precursor solution was

prepared by dissolving 2mmol of Bismuth (111) nitrate $(Bi(NO_3)_3.5H_2O)$ into 5ml ethylene glycol solution was hot injected into the flask. The reaction continued at 140ºC after 1 hour and then the reaction solution was slowly cooled down to room temperature. Finally, the products were collected by centrifugation and washed with distilled water and ethanol several times. Finally, dried the sample was dried under vacuum at 100°c for 12 hours. The overall yield of the Bi_2Te_3 nanoparticles calculated from the starting precursors was estimated to be as high as 93%, which truly demonstrated the potential for scaling-up of this simple and straightforward synthetic approach for synthesis of mass production.

X-ray diffraction (XRD) data were obtained with a powder diffractometer (Bruker's AXS modal D_8 advanced system used carry out the XRD experiment). Using unfiltered Cu Kα radiation (λ = 1.5406 Å) at 45 kV and 40 mA. The contribution from Kα_2 radiation was stripped using a Ni filter, energy dispersive spectroscopy detector (EDS) for compositional analysis. Scanning Electron Microscopy (SEM) was performed using a JEOL JSM-6700F. Morphological studies were carried out using field-emission scanning electron microscope (FESEM) (Model Zeiss Ultra55), transmission electron microscope (TEM) images, selected area electron diffraction (SAED) patterns (Model FEI Technai G^2 S-Twin).

III. RESULTS AND DISCUSSIONS

Fig.1(a-c) shows the FESEM images of the synthesized nanoparticles and nanowires of Bi_2Te_3. It was observed from Fig. 1 (c) that clearly spherical Bi_2Te_3 nanoparticles with a homogeneous size distribution of 10-20 nm were synthesized with the presence of N_2. Fig. (a) and (b) show the FESEM images of nanoparticles decorated Bi_2Te_3 nanowires. It was confirmed that the average size of the nanoparticles decorated nanowires length is several micrometers and diameter is 16-20nm without the presence of N_2.
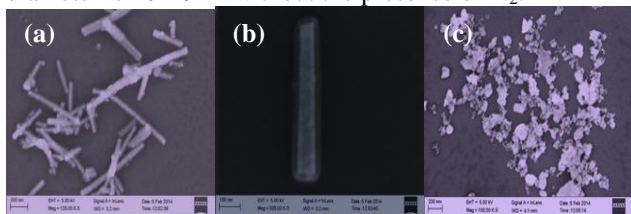

Fig. 1 SEM images of Bi_2Te_3 (a,b,) nanowires (c) nanoparticles

Fig. 2 (a) and (b) shows the XRD spectrums of Bi_2Te_3 nanoparticles and nanowires respectively. Both the cases hexagonal-phase Bi_2Te_3 (JCPDS_65-3750) was observed.

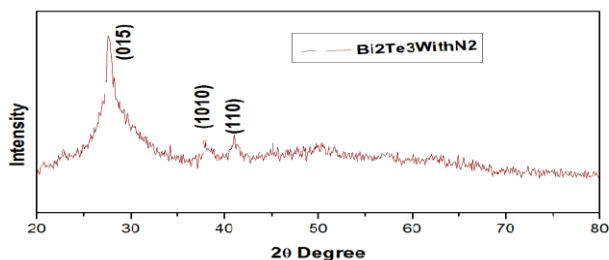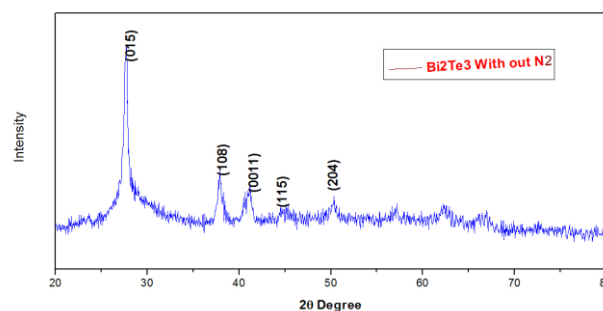Figure 2(a) The XRD pattern of the Bi_2Te_3 Nanoparticles (With N2)

Figure 2(b) The XRD pattern of the Bi_2Te_3 Nanowires (with outN2)

Fig. 3(a) and (b) shows the EDS spectra of Bi_2Te_3 nanoparticles and nanowires respectively. The atomic composition ratios of the bismuth telluride nanoparticles and nanoparticles decorated nanowires are ratio of 37:40 and 36:45 and which well corresponds to the stoichiometric composition of Bi_2Te_3.

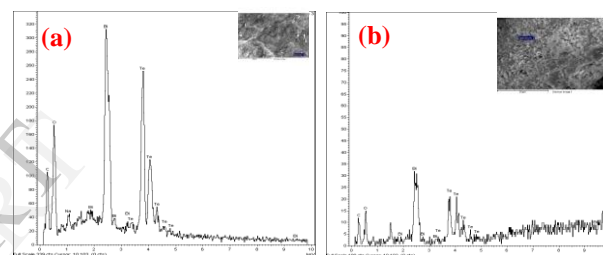Fig.3 (a) The EDS analysis of the Bi_2Te_3 Nanoparticles, atomic ratio of Bi_2: Te_3 37:42. (b) The EDS analysis of the Bi_2Te_3 Nanowires, Bi_2:Te_3 atomic ratio of 36:45.

Fig. 4(a) and (b) show the TEM images Bi_2Te_3 nanowires and nanoparticles respectively. It was confirmed from Fig. 4 (a) and (b) that Bi_2Te_3 nanowires and nanoparticles were synthesized having higher aspect ratio nanowires by controlling the synthesis by N_2 during the rational synthesis method.
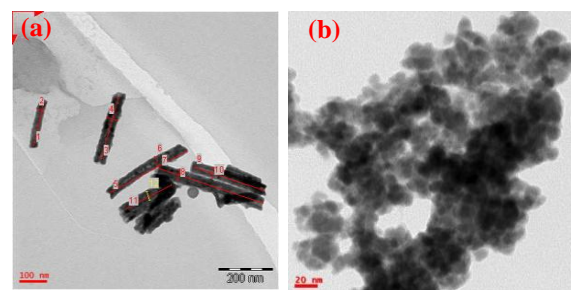

Fig. 4. TEM images of Bi_2Te_3 (a) nanowires (b) nanoparticles

CONCLUSIONS

Both nanowires and nanoparticles of Bi_2Te_3 were synthesized by using the rational chemical synthesis method. From the FESEM and TEM analysis, it was revealed that the nanoparticles were obtained when N_2 was introduced during the synthesis whereas nanowires in the absence of N_2 during the synthesis process. Preliminary experimental results revealed that nanoparticles were grown when N_2 was introduced as a protection gas whereas nanoparticles decorated nanowires were observed without the presence of N_2. Such findings will provide a pathway to control the morphology of the Bi_2Te nanostructured thermo electric materials having higher aspect ratios for future thermoelectric devices applications for future energy harvesting applications.

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