Solvothermal Synthesis and Characterization of Bi_2O_3Nanoparticles

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Abstract. In this paper,bismuth oxide (Bi_2O_3)nanoparticleswere fabricated by a facilesolvothermal process with the presence of ethylene glycol and further calcination.Theresultant products were characterised by thermogravimetric analysis, powder X-ray diffraction, scanning electronmicroscope.The results show that bismuth oxide nanoparticleswith a diameter ofabout 50–100 nm were prepared using ethylene glycolandethyl alcohol as solvent, the solvothermal reaction took place at 120°Cin 10 h.The increaseof annealing temperatures lead to thetransformation from tetragonal phase to monoclinic phase of bismuth oxides, and the phenomenon of agglomeration was observed, with particle size increased as well.Bismuth oxide nanoparticles annealed at 300 °Cand 350°Ccontain thehighest intensity of tetragonal and monoclinicphaseof bismuth oxides.

Introduction

Bismuth oxide(Bi_2O_3) has received considerable attention over the last three decades. It is well known that bismuth oxide has sixpolymorphic forms, denoted by α-Bi_2O_3(monoclinic), β-Bi_2O_3(tetragonal), γ-Bi_2O_3 (body centered cubic), δ-Bi_2O_3 (face centered cubic)[1], ε-Bi_2O_3 (orthorhombic)[2] and ω-Bi_2O_3(triclinic)[3], respectively.Among them, the low-temperature α-phase and the high-temperature δ-phases are stable, but the others are high-temperature metastable phases[4]. What's more,it hasa lot ofpeculiar physical and chemical properties, such as a wide energy gap change (from 2 to 3.96 eV)[5], high oxide-ion conductivity properties (1.0S/cm)[6], high refractiveindex($n_{\delta-Bi2O3}$=2.9)[7], dielectric permittivity(ε_r=190), besides excellent photoconductivity and photoluminescence[8]. Due to its peculiar properties, bismuth oxide hasbecome one of the important functional materials which has been applied in a wide range of areas,such as solid oxide fuel cells[6], gas sensors[9], photocatalysts[10], energetic materials[11]and others. For the above mentionedapplications,crystal forms, particle structure and size and specific surface area are very important.

Recently, bismuth oxide havebeen synthesized through different methods,such as co-precipitation[12],sol-gel method[13], chemical vapor deposition[14], microwave-assisted method[15]. In addition, differentBi_2O_3 nano/microstructures have been synthesized, such as nanoparticles[16], nanowires[17], nanorods[18], thin films[19] and so on. Compared with the above synthesis techniques,hydrothermal has been proved to be a very useful method in synthesizing nanostructures of inorganic functional materials[20],and the hydrothermallysynthesizedpowders offer many advantages, such as high degreeof crystallinity, well-controlled morphology, high purity and narrow particle size distribution.

The aim of this paper is to synthesize bismuth oxide nanoparticles and control the phase structure and morphology by a facilesolvothermal process with the presence of ethylene glycol at low temperature and further calcination.Product properties such as the morphology and phase structure and transformations, as well as the effect of calcination were studied.

Experiment

Materials. All reagents used in this study were of analytical grade and were purchasedwithout further purification.Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$)was received from Sinopharm Chemical Reagent Co., Ltd.Ethylene glycol ($(CH_2OH)_2$) waspurchased from Tianjin Fu Chen Chemical Reagents Factory.Absoluteethyl alcohol (CH_3CH_2OH) was purchased from Beijing Chemical Factory. Deionized water was prepared in our own laboratory.

Preparation of bismuth oxide nanoparticles. Bismuth oxide nanoparticles was prepared by a facile solvothermal process with the presence of ethylene glycol (EG) and further calcination.In a typical preparation procedure, 2.425g of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in a100mL beakercontaining 10mL EG under magnetic stirringuntil it has dissolved, and the hydrolyzation of bismuth nitrate pentahydrate could be prevented. And then 30mL of absolute ethyl alcoholwas added in the above solution underconstantlystirring for 1 h, and then the transparent solution was formed. The above mixed solution was transferred intoa stainless steel autoclave with a Teflon linerof 50 mL capability, and heated upto 160 °C for 10 h. After theautoclave was cooled to room temperature naturally, the as-formedprecipitates were filtered, and washed several times with deionized water and absolute ethyl alcohol before it was dried in the air at 70 °C for 12 h. This precursorwas subjected to differential thermal analysis and thermogravimetric analysis (TG/DTA6300, SII Nano Technology Inc., Japan) in order to establish a thermal treatment schedule.

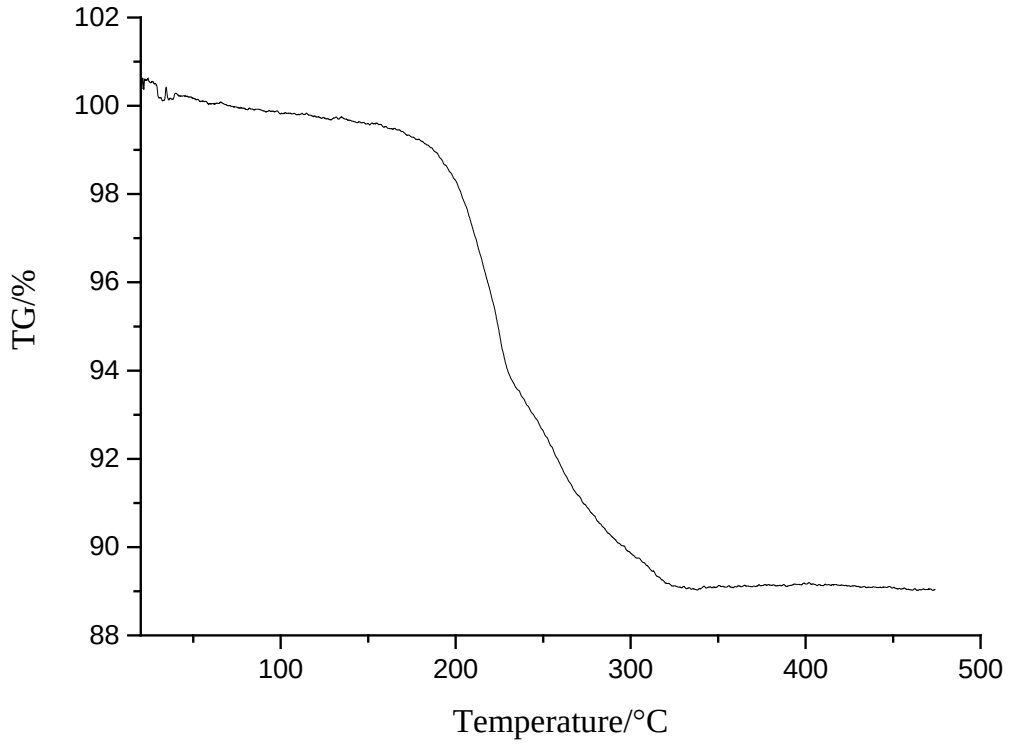

Fig.1TG curve of the as prepared precursor

According to the TG results (Fig.1), the precursor were transferred into ceramic crucibles with covers, and introduced into a muffle furnace heated up to 275 °C, 300 °C, 325 °C and 350 °C for 2 h with a heating rate of 5 °C min^{-1} to decompose precursor into Bi_2O_3, respectively.

Characterization. The crystal phase structure and phase purity of the as-synthesized bismuth oxide nanoparticles werecharacterized by X-raydiffraction (XRD, Bruker D8 advance) using a Cu Kα (λ=1.54056Å). The scans were taken at room temperature over a wide range of 2θ=($20^o - 70^o$) at

0.02 degrees intervals. The morphologies and structure analysis of the as-preparedproducts were observed on scanning electron microscope (SEM, Hitachi S4800).

Results and discussion

Analysis of XRD results. The powder X-ray diffraction (XRD) patterns of bismuth oxide nanoparticles annealed at different temperatures areillustrated in Fig.2.It can be seen fromthe spectra that the bismuthoxide annealed at275 °Cand 300°Care absolutely composed of tetragonal phase of bismuth oxide (β-Bi_2O_3) with the lattice parameters of$a$=b=7.741 Å and c=5.634 Å, no other impurity peaks were detected,which are completely consistentwith JCPDS NO. 78-1793.The crystallinity of the products powders was calculated by the equation C=(P/T)100%. C is the degree of crystallinity; P the diffraction peak intensity and T the total intensity.The calculated crystallinity of the products annealed at 275 °Cand 300 °C were 94% and 100%, respectively. The results suggest that heat treatment at300 °C for 2 h was favorable for the complete formation of β-Bi_2O_3.The as annealed products with calcination temperature of 325 °Care mainly composed of the most stable monoclinic phase of bismuth oxide (α-Bi_2O_3)(JCPDS NO. 76-1370). It was also observed that the weaker characteristic peak of β-Bi_2O_3 appeared in the XRD pattern, which indicates that the α phase of bismuth oxide accounts for most of the proportion of the sample and only a small percentage of the sample is β-Bi_2O_3.For the calcination temperature of 350 °C, the characteristic peak of β-Bi_2O_3 disappeared and the calculated crystallinity was 100%.We can conclude that the phase of the products transformed from tetragonal phase to monoclinic phase at the heat treatment of 300–350 °C. Therefore the Bi_2O_3 nanoparticles with the twocrystal structures could be selectively prepared under presentexperimental conditions.Their morphologies and surface structures were then studied by SEM.

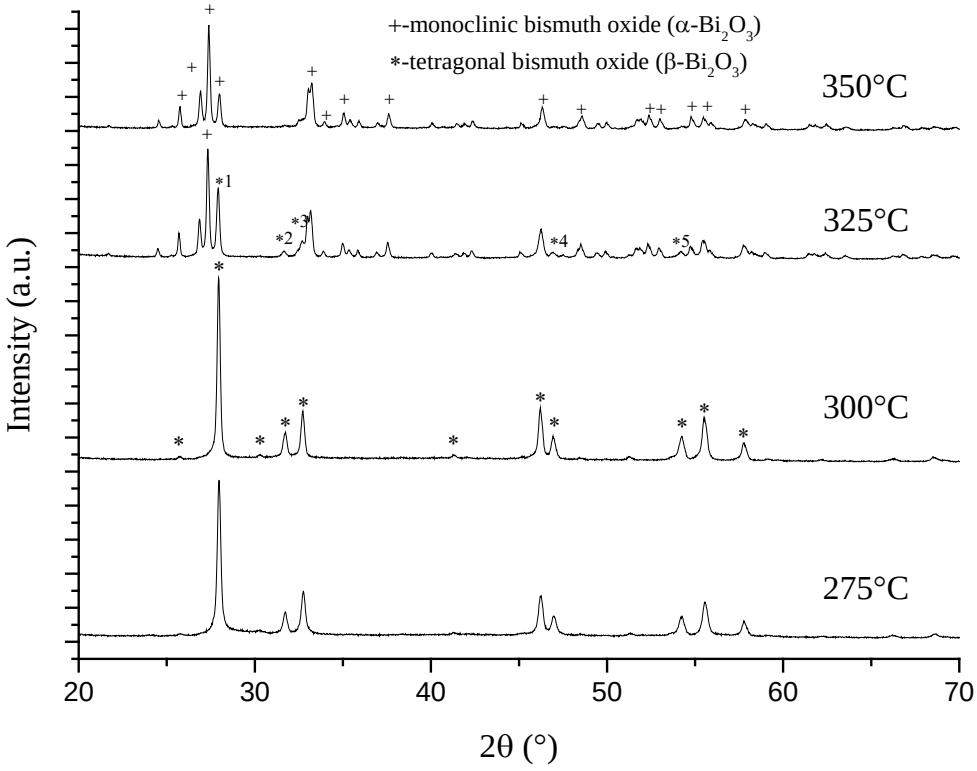

Fig.2 XRD patterns of bismuth oxide nanoparticles annealed at different temperatures

Analysis of SEM results. The SEM micrographs ofthe bismuthoxidesnanoparticles annealed at different temperaturesare shown in Fig.3. Fig.3(a) shows a typical high-magnification SEM image

of the products obtained by calcination after the solvothermal treatment, and it can be noticed that the morphology of the bismuthoxides particles are mainly spherical and contain a little nanosheets,the morphology is homogeneous in general. The particle size is about 50nm and increased to 100 nm with the calcination temperature increasing to 350 °C. It can be also found that the agglomeration of nanoparticles isincreased with the increase of calcination temperature. Therefore β-Bi_2O_3 withan average diameter of 50 nm and α-Bi_2O_3 of 100 nm could be obtained by the changing calcination temperature.

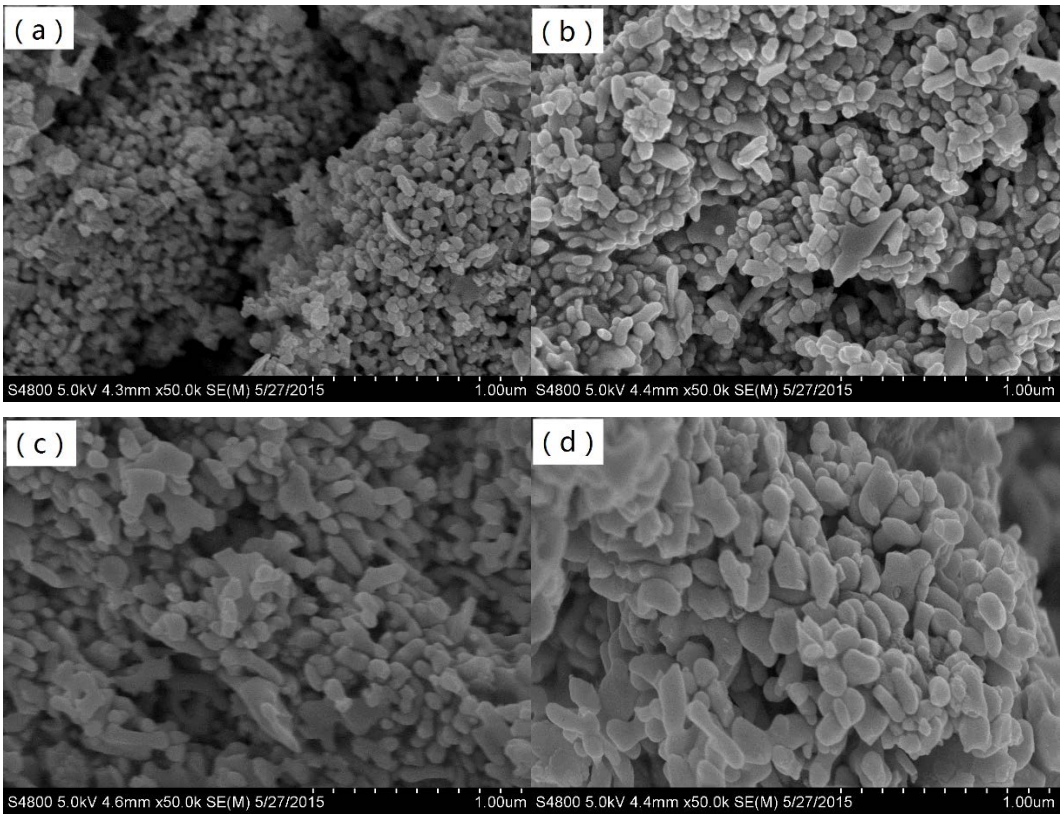

Fig.3 SEM photographs of bismuth oxide nanoparticles annealed at 275℃ (a), 300 °C (b), 325 °C (c) and 350 ℃ (d), respectively.

Formation mechanism. The SEM micrographs ofthe as obtained precursor from 10h solvothermal reactionis shown in Fig.4.It can been seen that precursor nanosheets with an edge lengthof 200–300 nm and thickness of 10 nm were synthesizedby a solvothermalprocess for 10 h. The nanosheets aggregated together and the nanostructrure is hierarchical flower-like. The nanosheets would be transformed into nanoparticles as show in Fig.3(a) after calcination. Based on the above experimental results, we considered thatthe formation of the nanoparticles was a cooperation effect of Ostwaldripening and calcination process[21].A possible formation process is schematically illustrated in Fig.5. Firstly, $Bi(NO_3)_3$dissolved in the mixed solution and Bi^{3+}reacted with ethylene glycol to form a relatively stable$Bi_2(OCH_2CH_2O)_3$ complex because of the strong coordinationwithBi^{3+}[22], and Bi_2O_3 nucleus formed through the hydrolysation ofthe most of $Bi_2(OCH_2CH_2O)_3$ in solution.Then the nucleus grew along the 2D direction,resulting in the formation of the nanosheets. Meanwhile, some $Bi_2(OCH_2CH_2O)_3$without hydrolysis were doped in the nanosheets. Finally, thecalcination at 300 °C and 350 °C of precursor nanosheets led to the formationof high crystalline β-Bi_2O_3 and α-Bi_2O_3, respectively.

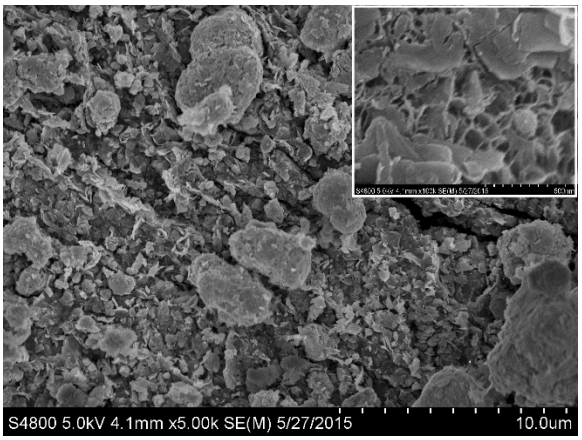

Fig.4 SEM image of the as obtained precursor from 10h solvothermal reaction

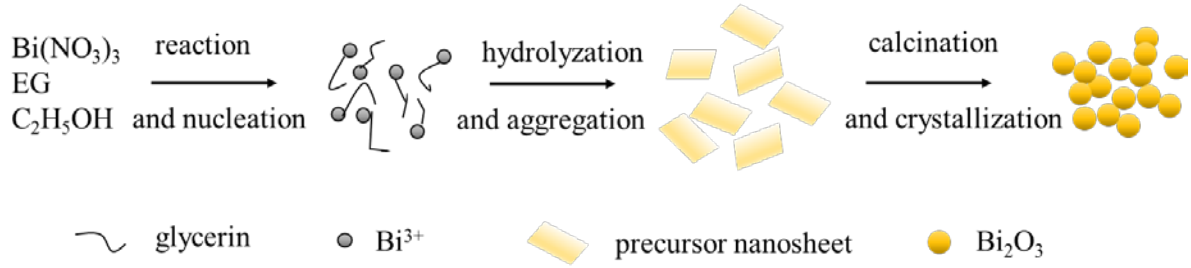

Fig.5Schematic illustration of the possible formation mechanism ofBi_2O_3 nanoparticles

Conclusions

Bismuth oxidesnanoparticles were prepared by a facile solvothermal process with the presence of ethylene glycol and further calcination at different temperatures.Differentcalcination temperatures lead to different intensities of tetragonal andmonoclinic phases of bismuth oxides. The β-Bi_2O_3 with an average diameter of 50 nm could be obtained after the further calcination at 300 °C. While α-Bi_2O_3 with an average of 100nm could be formed with the calcination temperature increasing to 350 °C.

Acknowledgements

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