Solvothermal Synthesis and Characterization of Bi$_2$O$_3$ Nanoparticles

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Abstract. In this paper, bismuth oxide (Bi$_2$O$_3$) nanoparticles were fabricated by a facile solvothermal process with the presence of ethylene glycol and further calcination. The resultant products were characterised by thermogravimetric analysis, powder X-ray diffraction, scanning electron microscope. The results show that bismuth oxide nanoparticles with a diameter of about 50−100 nm were prepared using ethylene glycol and ethanol as solvent, the solvothermal reaction took place at 120°C in 10 h. The increase of annealing temperatures lead to the transformation 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 °C and 350°C contain the highest intensity of tetragonal and monoclinic phase of bismuth oxides.

Introduction

Bismuth oxide (Bi$_2$O$_3$) has received considerable attention over the last three decades. It is well known that bismuth oxide has six polymorphic forms, denoted by α-Bi$_2$O$_3$ (monoclinic), β-Bi$_2$O$_3$ (tetragonal), γ-Bi$_2$O$_3$ (body centered cubic), δ-Bi$_2$O$_3$ (face centered cubic)[1], ε-Bi$_2$O$_3$ (orthorhombic)[2] and ω-Bi$_2$O$_3$ (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 has a lot of peculiar physical and chemical properties, such as a wide energy gap change (from 2 to 3.96 eV)[5], high oxide-ion conductivity properties (1.0 S/cm)[6], high refractive index ($n_\delta$-Bi$_2$O$_3$=2.9)[7], dielectric permittivity($\varepsilon_r$=190), besides excellent photoconductivity and photoluminescence[8]. Due to its peculiar properties, bismuth oxide has become 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 mentioned applications, crystal forms, particle structure and size and specific surface area are very important.

Recently, bismuth oxide have been synthesized through different methods, such as co-precipitation[12], sol-gel method[13], chemical vapor deposition[14], microwave-assisted method[15]. In addition, different Bi$_2$O$_3$ 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 hydrothermally synthesized powders offer many advantages, such as high degree of 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 purchased without further purification. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) was received from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol ((CH₂OH)₂) was purchased from Tianjin Fu Chen Chemical Reagents Factory. Absolute ethyl alcohol (CH₃CH₂OH) 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, 2.425 g of Bi(NO₃)₃·5H₂O was dissolved in a 100 mL beaker containing 10 mL EG under magnetic stirring until it has dissolved, and the hydrolyzation of bismuth nitrate pentahydrate could be prevented. And then 30 mL of absolute ethyl alcohol was added in the above solution under constant stirring for 1 h, and then the transparent solution was formed. The above mixed solution was transferred into a stainless steel autoclave with a Teflon liner of 50 mL capability, and heated up to 160 °C for 10 h. After the autoclave was cooled to room temperature naturally, the as-formed precipitates 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 precursor was subjected to differential thermal analysis and thermogravimetric analysis (TG/DTA6300, SII Nano Technology Inc., Japan) in order to establish a thermal treatment schedule.

![TG curve of the as-prepared precursor](image)

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 Bi₂O₃, respectively.

Characterization. The crystal phase structure and phase purity of the as-synthesized bismuth oxide nanoparticles were characterized by X-ray diffraction (XRD, Bruker D8 advance) using a Cu Kα (λ=1.54056 Å). The scans were taken at room temperature over a wide range of 2θ=(20°–70°) at
0.02 degrees intervals. The morphologies and structure analysis of the as-prepared products 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 are illustrated in Fig. 2. It can be seen from the spectra that the bismuth oxide annealed at 275 °C and 300 °C are absolutely composed of tetragonal phase of bismuth oxide (β-Bi$_2$O$_3$) with the lattice parameters of $a=b=7.741$ Å and $c=5.634$ Å, no other impurity peaks were detected, which are completely consistent with JCPDS NO. 78-1793. The crystallinity of the products powders was calculated by the equation $C=\frac{P}{T}\times 100\%$. $C$ is the degree of crystallinity; $P$ the diffraction peak intensity and $T$ the total intensity. The calculated crystallinity of the products annealed at 275 °C and 300 °C were 94% and 100%, respectively. The results suggest that heat treatment at 300 °C for 2 h was favorable for the complete formation of β-Bi$_2$O$_3$. The as-annealed products with calcination temperature of 325 °C mainly composed of the most stable monoclinic phase of bismuth oxide (α-Bi$_2$O$_3$) (JCPDS NO. 76-1370). It was also observed that the weaker characteristic peak of β-Bi$_2$O$_3$ 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$_2$O$_3$. For the calcination temperature of 350 °C, the characteristic peak of β-Bi$_2$O$_3$ 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$_2$O$_3$ nanoparticles with the two-crystal structures could be selectively prepared under present experimental conditions. Their morphologies and surface structures were then studied by SEM.

![XRD patterns of bismuth oxide nanoparticles annealed at different temperatures](image)

**Analysis of SEM results.** The SEM micrographs of the bismuth oxide nanoparticles annealed at different temperatures are 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 50 nm and increased to 100 nm with the calcination temperature increasing to 350 °C. It can be also found that the agglomeration of nanoparticles is increased with the increase of calcination temperature. Therefore β-Bi₂O₃ with an average diameter of 50 nm and α-Bi₂O₃ of 100 nm could be obtained by the changing calcination temperature.

![Fig.3 SEM photographs of bismuth oxide nanoparticles annealed at 275°C (a), 300 °C (b), 325 °C (c) and 350 °C (d), respectively.](attachment:fig3.png)

**Formation mechanism.** The SEM micrographs of the as-obtained precursor from 10h solvothermal reaction is shown in Fig.4. It can been seen that precursor nanosheets with an edge length of 200–300 nm and thickness of 10 nm were synthesized by a solvothermal process for 10 h. The nanosheets aggregated together and the nanostructure 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 that the formation of the nanoparticles was a cooperation effect of Ostwald ripening and calcination process [21]. A possible formation process is schematically illustrated in Fig.5. Firstly, Bi(NO₃)₃ dissolved in the mixed solution and Bi³⁺ reacted with ethylene glycol to form a relatively stable Bi₂(OCH₂CH₂O)₃ complex because of the strong coordination with Bi³⁺ [22], and Bi₂O₃ nucleus formed through the hydrolysis of the most of Bi₂(OCH₂CH₂O)₃ in solution. Then the nucleus grew along the 2D direction, resulting in the formation of the nanosheets. Meanwhile, some Bi₂(OCH₂CH₂O)₃ without hydrolysis were doped in the nanosheets. Finally, the calcination at 300 °C and 350 °C of precursor nanosheets led to the formation of high crystalline β-Bi₂O₃ and α-Bi₂O₃, respectively.
Conclusions

Bismuth oxides nanoparticles were prepared by a facile solvothermal process with the presence of ethylene glycol and further calcination at different temperatures. Different calcination temperatures lead to different intensities of tetragonal and monoclinic phases of bismuth oxides. The $\beta$-Bi$_2$O$_3$ with an average diameter of 50 nm could be obtained after the further calcination at 300 °C. While $\alpha$-Bi$_2$O$_3$ with an average of 100 nm could be formed with the calcination temperature increasing to 350 °C.

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