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Short communication

Synthesis of bismuth oxide nanoparticles by the polyacrylamide gel route

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Abstract

A polyacrylamide gel route has been adopted for the preparation of bismuth oxide nanoparticles. Thermal behaviour of the polyacrylamide gel has been studied by means of thermogravimetry (TGA). The formation of monoclinic Bi_2O_3 nanocrystallites is confirmed by X-ray diffraction (XRD). Transmission electron microscopy (TEM) investigation revealed the average particle size of Bi_2O_3 nanoparticles to range from 30 nm to 50 nm.

Keywords: A. Polyacrylamide gel; B. Bismuth oxide; C. Nanoparticles

1. Introduction

Nanocrystalline particles generally display properties different from their bulk counterparts from which they are derived. Due to their unique physical and chemical properties, bismuth oxide nanoparticles have been used widely as an important component in the field of solid oxide fuel cells, gas sensors, varistors, electric and optical materials, high temperature superconductor materials, functional ceramics and catalysts, etc. [1,2]. Many chemical methods have been employed to prepare Bi_2O_3 nanoparticles, e.g. precipitation [3,4], flame spray pyrolysis [5], and sol–gel methods [6–9].

How to control the preparation steps is the key point of obtaining high quality nanoparticles with nanosize-dependent properties; sol–gel processing has been proved to control the material structure on a nanometer scale from the earliest stages of processing [10,11]. Many novel sol–gel methods have been developed recently. In 1989, a polyacrylamide gel process was described by Douy and Odier [12] for preparing three different ultrafine powders: $YBa_2Cu_3O_{7-x}$, $2SiO_2$–$3Al_2O_3$ and $LaAlO_3$, and then Liu et al. [13] also reported the synthesis of the LSGM materials by the acrylamide polymerization technique. This polymer gel method has attracted more and more attention and has been used to prepare many different oxide nanoparticles, metallic and oxide compounds, such as ZnO [14], Al_2O_3 [15], In_2O_3 [16], $NdFe_{10}Mo_2$ [17] and $Ce_{1-x}Bi_xO_{2-x/2}$ solid electrolytes [18]. With polymeric chains forming a network, metal ions are entrapped evenly within the polyacrylamide gel, which is helpful for forming uniform oxide nanoparticles. Stepto Robert et al. [19] have introduced the theory about the formation, structure and properties of polymer networks. This polymer gel method differs from traditional preparation technique in two aspects: (a) no expensive alkoxide reactants are necessary and (b) relatively lower calcination temperature. We here report polymer gel process for the preparation of nanocrystalline Bi_2O_3.

2. Experimental

Bismuth nitrate and standard ammonium hydroxide solution, ammonium persulphate, acrylamide, *N*,*N*′-methylenebisacrylamide and citrate used are of AR grade. Desired quantities of citrate, acrylamide, *N*,*N*′-methylenebisacrylamide and ammonium persulphate as catalyst were added in turn to the dilute nitric acid solution of bismuth nitrate with concentration (Bi^{3+}: 0.05 mol/l). $NH_3 \cdot H_2O$ solution (1:1) was dropped into the mixing solution until the pH value reached 9. The mixture was stirred with water bath at room temperature, and then the

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mixing solution turned into gel at 60 °C with the slow increase of water bath temperature. The gel was dried at 120 °C for 48 h in vacuum drier. The xerogel thus formed was calcined in a tube furnace in air atmosphere at 460 °C for 4 h to obtain light yellow powder. The xerogel was studied by TGA (NETZSCH STA 449C) to define the precise calcination temperature. The X-ray diffraction (XRD) pattern was recorded by using a Japan Rigaku D/max-IIIA diffractometer with filtered Cu Kα radiation. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 20° to 60° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with Philips CM-300 instrument at the accelerating voltage of 200 kV. The ultrafine powders were sonically dispersed in amyl acetate for 1 h and were dropped and dried on a carbon-coated TEM copper grid.

3. Results and discussion

Typical TG curve for decomposition of the xerogel at a heating rate of 10 K/min in atmosphere is shown in Fig. 1.

TG curve in Fig. 1 indicates a weight loss of 76.5% occurred from ambient to 450 °C, which results from the dehydration and decomposition of the organic polymer, nitrate, etc. This value agrees well with the theoretical mass of the organic (76.83%) used in the reaction. Little change in the TG curve can be observed after 460 °C, which reveals that the bismuth polyacrylamide gel decomposed to yield bismuth oxide only at 460 °C, so here we choose 460 °C as the calcination temperature. The calcination temperature is remarkably lower than that used in the traditional precipitation method.

The XRD pattern of the obtained sample readily indexed Bi_2O_3 with monoclinic structure (JCPDS 41-1449). The broadened diffraction peaks which are observed indicate that the crystalline size of sample is very fine. The crystallite sizes were calculated by Debye–Scherrer equation, $D = k\lambda/\beta \cos\theta$, where D is the crystallite size, k is equal to 0.89 as a constant assuming that the particles are spherical, λ is the wavelength of the X-ray radiation ($\lambda = 0.15418$ nm), β is the line width obtained after elimination of the instrumental broadening and θ is the angle of diffraction. Bismuth oxide exists as two stable forms (monoclinic α-Bi_2O_3 and cubic-Bi_2O_3) and two other metastable phases (tetragonal β-Bi_2O_3 and bcc γ-Bi_2O_3), which can be converted to each other at certain conditionn [20]. The crystalline pattern of powders and the observed d-lines match the reported values for α-Bi_2O_3 phase.

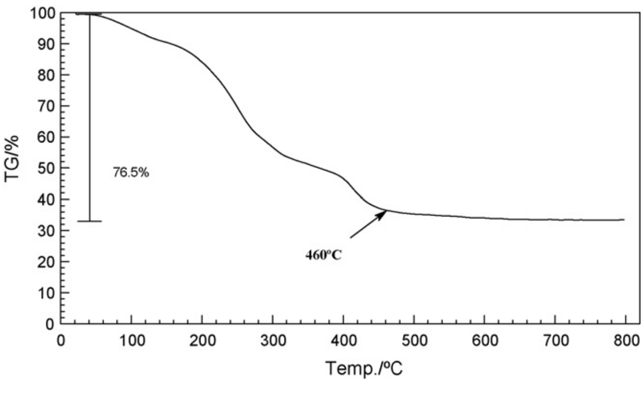

Fig. 1. TG curve of the xerogel prepared with 0.05 mol/l starting concentration of bismuth nitrate solution.

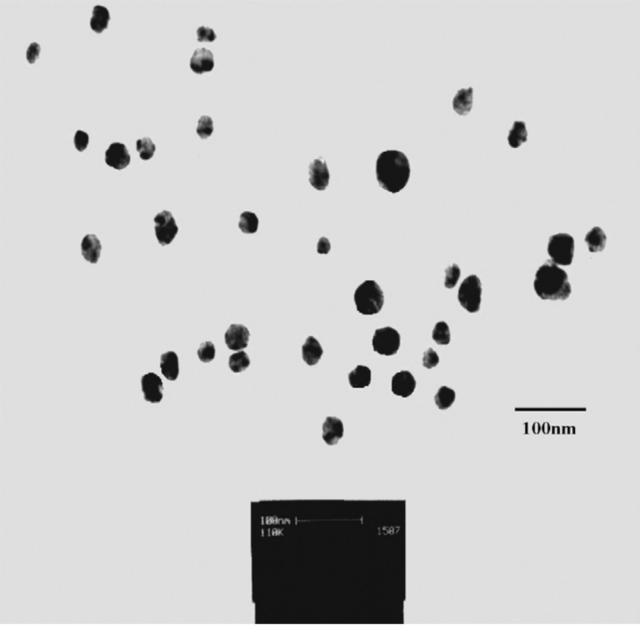

Fig. 2. TEM picture of the sample calcined at 460 °C for 4 h.

Table 1
Summary of the crystallite size, the calculated lattice parameters of the synthesized sample

Sample	The average crystallite size (nm)	The calculated lattice parameters		The literature lattice parameters	
		a	*c*	*a*	*c*
1	37.89	5.8506	7.5171	5.8499	7.5123

The average crystalline size and lattice parameters of the synthesized powders were calculated and are shown in Table 1.

The calculated lattice parameters by least squares method are in good agreement with literature data reported for the α-Bi_2O_3 phase (JCPDS 41-1449), which also confirm that the synthesized powders are monoclinic Bi_2O_3 nanocrystallites.

The TEM image of the superfine Bi_2O_3 powder (Fig. 2) shows that Bi_2O_3 nanoparticles are well dispersed without evident agglomeration. The particles are of ellipsoid-like shape, and the average particle size varies from 30 nm to 50 nm, which was in good agreement with the XRD result.

4. Conclusions

A polyacrylamide gel process was used for the preparation of bismuth oxide nanoparticles. The precise calcination temperature of 460 °C is much lower than for the traditional precipitation method. The Bi_2O_3 nanocrystallite is in monoclinic form, and the average size of these nanoparticles ranges from 30 nm to 50 nm.

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