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Study on preparation and characterization of uniform bismuth nanospheres

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The uniform and monodisperse bismuth nanospheres were successfully prepared by simple and convenient solvothermal method. The bismuth nitrate was reduced by ethylene glycol at 150-200 °C for 20-30 hrs. The nanospheres were characterized by powder X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The dispersivity of bismuth nanospheres was investigated using optical microscope. The optimum reaction conditions to prepare the uniform bismuth nanospheres with a narrow diameter range was investigated. The results indicate that the monodisperse bismuth nanospheres prepared at 200 °C possess sizes ranging from 100-200 nm. The formation mechanism of the bismuth nanospheres was hypothesized.

Key words: Bismuth, Nanospheres, Solvothermal, Monodisperse.

Introduction

Bismuth (Bi) has been extensively studied for its quantum transport and size effects behavior [1, 2]. Bi nanomaterials especially have received growing interests because of large magnetoresistance, finite-size effects, and enhanced thermal conductivity [3-5]. In recent years, Bi and its corresponding alloys have attracted much attention, because they would be promising anode materials for sodium ion batteries (SIBs) [6] and lithium ion batteries (LIBs)[7]. Nano-sized Bi-based catalyst electrodeposited on a Cu foil is used as a cathode for electrochemical reduction of CO_2 to formate in aqueous solution[8]. The Bi nanoparticles can act as intermediate in the synthesis of nanostructured Bi_2Te_3 and catalyst during the growth of CdS quantum wires [9-11].

Wide varieties of Bi nanostructures such as nanoparticles, nanowires, nanorods, nanotubes, triangular nanoplates, nanocubes, have been prepared by different methods [12]. The monodisperse metal spheres with low melting points such as Bi, Pb and In have been synthesized via simple solution-phase synthesis routes [13, 14]. Ethylene glycol (EG) is usually used as both solvent and reducing agent in the presence of polyvinyl pyrrolidone (PVP) [12, 15-17]. The solvothermal process is an important approach to prepare bismuth nanospheres, because of the simple synthetic route and low cost over other methods. However, controlling the size of the Bi nanospheres is still difficult and needs to be optimized. Futhermore, obtaining monodisperse partciles with narrow diameter 150 nm is motivated to carry out this research because of suitability of this size for the use in X-ray free electron laser (XFEL) experiment, a cutting edge tool to identify the structure of the nanoparticle [18].

In this paper, homogeneous and monodisperse Bi nanospheres were successfully prepared by simple solvothermal process. The nanospheres were characterized by XRD, SEM and TEM analysis. The dispersivity of particle is important in the XFEL experiment and it has been investigated by optical microscope. The formation mechanism of the bismuth nanospheres was hypothesized.

Experimental

All the reagents including nitric acid (HNO_3, 98 wt %), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), and ethylene glycol (EG), are analytical grade used without further purification.

0.5-0.75 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10-15 mL of 1 mol/L nitric acid, stirred at room temperature for 2 hrs. Then 40-50 mL EG was added slowly to the solution with vigorous stirring for several hours. EG plays a critical role as the solvent, reducing agent and capping agent in the absence of PVP in our synthesis. The final mixture was transferred into a stainless steel autoclave with Teflon liner. The autoclave was sealed, and then heated to 150-200 °C and maintained for 0-2 hr, i.e. a preheating process. Subsequently, it was cooled down to room temperature rapidly, and then heated to the same temperature as the preheating process and maintained for 20-30 hrs. After spontaneous cooling to room temperature, the obtained black solution was centrifuged to collect the powder which was then washed with plenty of absolute alcohol for 5-10 times. The final product was dried at 50 °C for

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two days under vacuum condition.

For monodisperse sample preparation, a small amount of black powder was dissolved in 1mL ethanol. Then mixture was sonicated 2 minutes to get deep black solution. Then 30 μL of black solution was pipetted out and added into 1-2 mL ethanol. The final solution was sonicated until get a homogeneous light gray solution. The solution of 2 μL was dropped to the cleansed glass slide, dried 5 minutes at room temperature.

The products were analyzed by X-ray diffractometer (Bruker D8 Advance) with Ni- CuKα ($\lambda = 1.54056$ Å) radiation at room temperature. The size, morphology and dispersivity of products were probed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800), transmission electron microscopy (TEM, JEM2100, Jeol) and optical microscope (KEYENCE, VHX-1000).

Results and Discussion

Fig. 1 shows the powder XRD patterns of the samples synthesized at 160 °C, 180 °C and 200 °C for 20 hrs. All the diffraction peaks could be readily indexed to the rhombohedral phase of bismuth. The XRD patterns are consistent with the (JCPDS card No. 05-0519). No peak of impurity was detected in the patterns indicating the high purity of the samples. The sharp and strong diffraction peaks confirm the high crystallinity of the Bi nanospheres.

The reaction time and temperature have significant effects on the morphology and size of the Bi

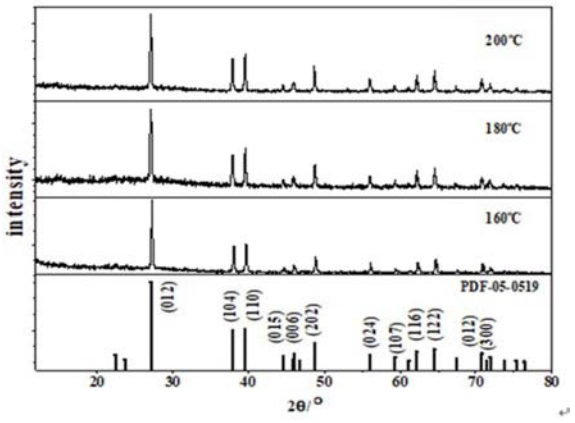

Fig. 1. XRD patterns of bismuth nanoparticles synthesized at different temperatures for 20 hrs.

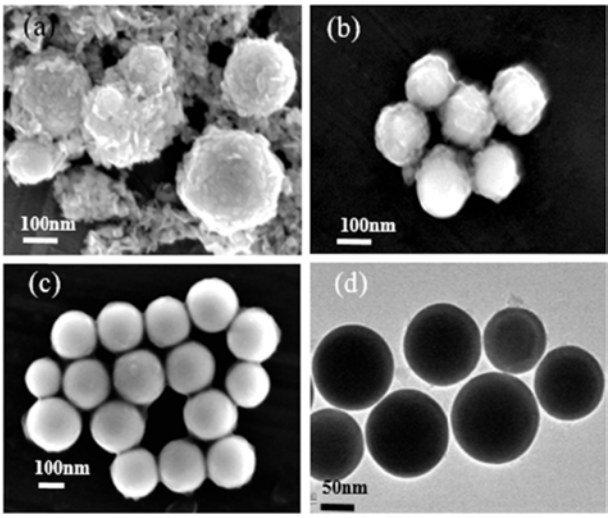

Fig. 2. The SEM (a-c) and TEM (d) images of bismuth nanospheres synthesized at different temperatures: (a) 160 °C; (b) 180 °C; (c, d) 200 °C.

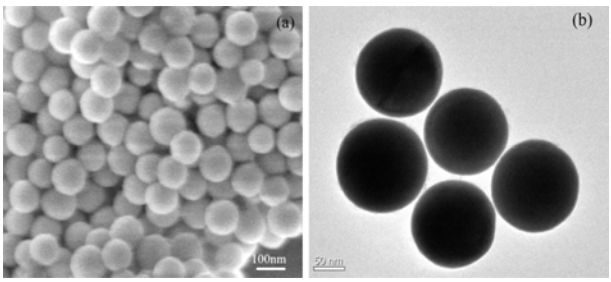

Fig. 3. The SEM and TEM images of Bi nanospheres synthesized at 200 °C using a preheating process.

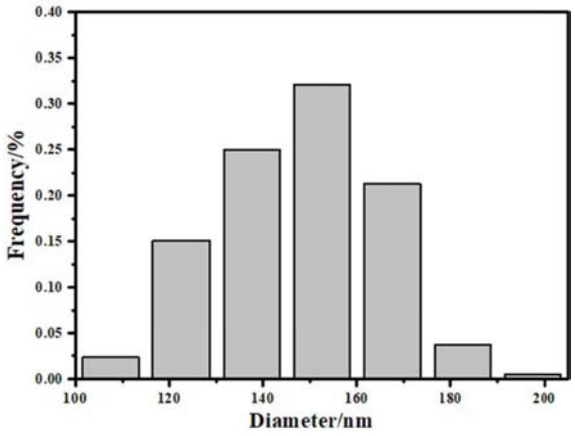

Fig. 4. The size distribution histogram of the Bi nanospheres synthesized at 200 °C using a preheating process.

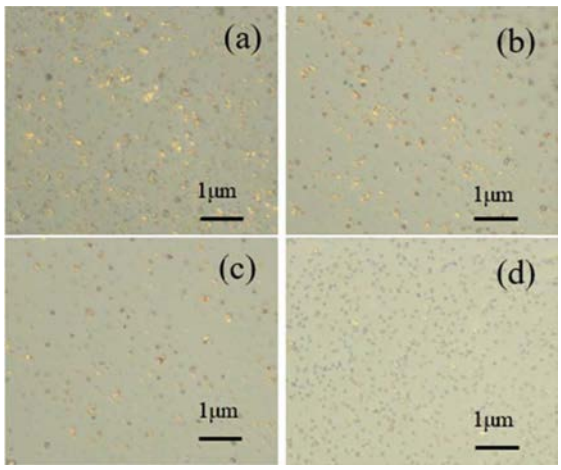

Fig. 5. Optical microscopy images of the dispersivity of Bi nanospheres sonicated for different time: (a) 5 minutes; (b) 10 minutes; (c) 20 minutes; (d) 30 minutes.

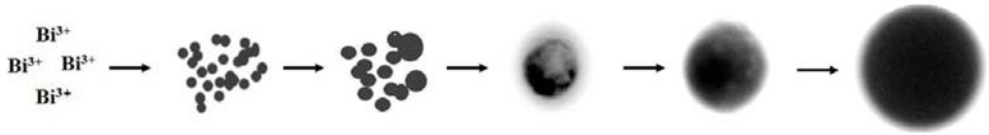

Fig. 6. Schematic illustrating of the formation mechanism of Bi nanospheres.

nanoparticles. Fig. 2 shows the SEM (a-c) and TEM (d) images of three samples synthesized at 160 °C, 180 °C and 200 °C for 30 hrs. The smooth and spherical Bi nanoparticles are synthesized at high temperature. The size of the particles is not uniform and show wide diameters range. The optimum solvothermal temperature to prepare the smooth and spherical Bi nanoparticles is 200 °C. It is observed that the surfaces of Bi nanospheres are covered by thin shells, which may be due to unreacted EG. Needless to say this, EG coatings can be removed from the surfaces by washing with plenty of ethanol [13].

The SEM and TEM images of Bi nanospheres synthesized at 200 °C for 28 hrs after preheating for 2 hrs are shown in Fig. 3. It can be seen that the uniform Bi nanospheres are with well-defined spherical structure and smooth surface. The sizes of Bi nanospheres are ranging from 100 to 200 nm as presented in Fig. 4. The histogram shows that Bi nanospheres have a narrow size distribution and the average diameter is about 147 nm. The preheating process plays an important role in preparing uniform Bi nanospheres. The optical microscopy images of the dispersivity of Bi nanospheres are presented in Fig. 5(a-d). The dispersive Bi nanospheres in solution are obtained by sonicating for 5, 10, 20 and 30 minutes. It can be seen that the sample sonicated for 30 minutes is highly monodispersed.

The formation mechanism of Bi nanospheres is schematically presented in Fig. 6. Firstly, Bi^{3+} is reduced in acid solution at high temperature using ethylene glycol. The Bi nuclei appear and aggregate led to form the Bi nanoparticles [19, 20]. The rapid aggregation of the Bi nuclei can be prevented to form different sizes of nanoparticles by preheating process. The nanoparticles grow into Bi nanospheres with roughly surface covered by the EG shells, then they disappear gradually by increasing the reaction time. The Bi nanospheres with well-defined and smooth surface are obtained.

Conclusions

In summary, the uniform bismuth nanospheres were successfully synthesized by facile solvothermal method. The ethylene glycol plays a critical role as the solvent, reducing agent and capping agent in the formation of bismuth nanoparticles. The reaction time and temperature have significant effect on the morphology and size of bismuth nanoparticles. Based on the experimental results, the optimum condition to obtain the nanospheres is solvothermal heating of 200 °C using a preheating process. The results indicated that the bismuth particles are solid nanospheres with smooth surface controlled by ethylene glycol, and the average size is about 147 nm with high monodispersity.

Acknowledgments

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