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Convenient solvothermal synthesis of nanoscale 0-2D Bi without surfactants and templates

Fengyu Kong [a,*], Wei Ning [b], Anding Wang [c,**], Yan Liu [b], Mingliang Tian [b]

[a] NingBo University of Technology, Ningbo, Zhejiang, China
[b] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, Anhui, China
[c] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, China

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ABSTRACT

Bi is a semimetal with unusual and attractive electronic properties. However, synthesis of nanoscale 0-2D Bi single crystal with good dispersity and quality without surfactants and substrates is still a challenge. In this paper, a novel, simple and low-cost solvothermal method for synthesis of 0-2D nanoscale Bi at mild conditions and without a surfactant/substrate is reported. By using $Bi(NO_3)_3 \cdot 5H_2O$ or $NaBiO_3 \cdot 2H_2O$ as Bi sources and environmental friendly $C_3H_8O_3$ as solvent, we synthesized nanospheres, nanowires and nanoribbons characterized with monodispersity, high purity and crystallinity. The growth mechanism of the 0-2D nanostructure was discussed. It is found that the Bi source, concentration and solvent significantly influences the morphology and size. Single crystal free-standing nanoribbon has large magnetoresistance up to 540% at 100 K. This novel approach can be applied in synthesis of nanostructured Bi single crystals and the large-scale fabrication of some other nanostructured semimetals.

1. Introduction

Morphologically distinct Bi nanomaterials have attracted enormous attention because of their unusual electronic properties [1] and potentially useful applications such as thermoelectric devices [2], optical devices [3], giant magnetoresistance (GMR) devices [4] and superconductivity devices [5]. In film samples with substrates, the unusual properties were found to be fundamentally different from those of common metals and were attributed to their highly anisotropic Fermi surface, small effective carrier masses and low carrier concentrations [1,4]. As well proved, the properties of nanostructured materials are seriously shape-dependent, especially in quasi one-dimensional structures, such as nanotubes, nanowires and nanoribbons [6]. Therefore, the synthesis of Bi with specific nanostructure has become a hot area of considerable interests.

To date, a range of techniques have been used for the preparation of Bi single crystals, especially the commonly used electrodeposition and solvothermal methods [7–11] for nanostructure material synthesis. Most of these studies manifest electrodeposition a popular technique for the formation of nanowires and nanotubes [12–16]. However, it is incapable for the synthesis of nanospheres and nanoribbons, because of the template limit, such as electrodeposition into porous membranes or by heterogeneous nucleation and growth at one-dimensional defects [17]. To some extent, template-based methods are limited, owing to requirements for template removal to obtain pure samples. The solvothermal method is accepted with wide applicability for nanostructured material synthesis. By introducing capping polymer poly(vinylpyrrolidone) (PVP) as a surfactant and a trace amount of Fe^{3+} to the reaction system, Wang etc. firstly prepared nanocubes, triangular nanoplates, nanospheres, and nanobelts using solvothermal with complicated reactions [10]. Other authors also synthesized nanostructured Bi and found the surfactant, substrate and the employed polymer stabilizer played important roles in controlling the size and morphology [7–9,18]. As listed in Table 1, all reported methods involve the reduction of Bi salts in the presence of organic surfactants or polymeric stabilizers at elevated temperature. These routes with complicated raw materials, surfactant and substrate are considerably beset by complicated process, time consuming and restriction of high-yield production [19,20]. Therefore, the development of mild, template-free, surfactant-free routes to produce 0-2D single-crystalline Bi remains a

* Corresponding author.
** Corresponding author.
E-mail addresses: fengyu.k@hotmail.com (F. Kong), anding@nimte.ac.cn (A. Wang).

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Table 1
Solvothermal synthesis methods of Bi nanostructures and related experiment parameters.

Precursor	Surfactant/template	T (°C)	t (h)	Morphology	Ref.
$NaBiO_3$ + ethylene glycol (EG)	Polyvinyl-pyrrolidone (PVP)	200	–	Triangular nanoplate; Cube	[10]
$NaBiO_3 \cdot 2H_2O$ + EG + $FeCl_3$		200	–	Ribbon	
$BiCl_3 \cdot 5H_2O$ + NaH_2PO_2		80	–	nanowire	[18]
$Bi[N(SiMe_3)_2]_3$ + $Na[N(SiMe_3)_2]$ + Tetrhydrofuran (THF)	Polymer-DIPB	180–210	15–17	dot, narrow ribbon	[7]
$Bi(NO_3)_3 \cdot 5H_2O$ + $NH_3 \cdot H_2O$	silicon template	180	24	Nanobelt	[9]
$Bi(NO_3)_3 \cdot 5H_2O$ + $C_3H_8O_3$	×	200	24	nanosphere	this study
$NaBiO_3 \cdot 2H_2O$ + $C_3H_8O_3$				0-2D	

challenge and are seriously desired.

Recently, we reported clear angular-dependent Shubnikov-de Haas (SdH) oscillations with 2D character, in high quality Bi nanoribbons with large surface-to-volume ratio samples [21,22]. The 2D surface characteristics were distinguished from transport properties because of the perfect planar surface, which were attractive for many groups. The new synthesis method, simply reported for nanoribbons [22], can be also used for preparation of controllable 0-2D Bi samples with high quality and different applications. In this study, we systematically reported the convenient solvothermal synthesis method of nanoscale 0-2D Bi without surfactant and substrate. According to the detailed investigation of the effects of synthesis parameters on size and shape of Bi samples, it is found that the size and morphology are significantly depended on the Bi ion concentration. The microscopic growth mechanisms of such structures and the atomic-scale growth kinetics were discussed.

2. Experiment procedures

2.1. Materials

Bi nanostructures were synthesized via a solvothermal approach using Bi nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR) or sodium bismuthate ($NaBiO_3 \cdot 2H_2O$, AR) as the starting material received from Aladdin. The solvent glycerin was purchased from Aladdin, used to prepare all solutions.

2.2. Synthesis of Bi nanospheres with $Bi(NO_3)_3 \cdot 5H_2O$

Bi nanospheres can be synthesized using Bi nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR) or sodium bismuthate ($NaBiO_3 \cdot 2H_2O$, AR) as the starting material. In a typical experiment, 0.1–0.5 g Bi nitrate was dispersed uniformly with magnetic force stirring in a 100 mL Teflon cup with 80 mL glycerin. The solution was bubbled with a flow of pure nitrogen gas for 10 min before the autoclave heated at 200 °C for 24 h. The precipitate formed was cooled to room temperature and then washed repeatedly with deionized water and alcohol. A grayish black product was recovered indicating the reduction of the white $Bi(NO_3)_3$ precursor to Bi.

2.3. Synthesis of Bi 0-2D samples with $NaBiO_3 \cdot 2H_2O$

Bi 0-2D samples were synthesized using sodium bismuthate ($NaBiO_3 \cdot 2H_2O$, AR) as the starting material. In a typical process, proper amount (0.01–0.2 g) of analytical-grade sodium bismuthate ($NaBiO_3 \cdot 2H_2O$) dissolved in 40 mL glycerol ($C_3H_8O_3$), vigorously stirred for 30 min, and then the solution was transferred to Autoclave with a capacity of 50 mL. Then the solution was bubbled with a flow of pure nitrogen gas for 10 min. After that, the autoclave was sealed and maintained at 200 °C for 24 h. After reaction, the resulting black solid product was collected by filtration and washed with ethanol to remove all of impurities.

2.4. Phase structure and morphology characterization analysis

The phase structure was detected by X-Ray diffraction (XRD) using a Rigaku-TTR3 instrument using Cu Ka radiation ($\lambda_{Cuk\alpha}$ = 1.5405 Å). The structural characteristics were investigated using a JEOL-2011 TEM. For HRTEM and selected area electron diffraction (SAED) observations, the nanostructures were dispersed in an alcohol solution and drop-cast onto a 300 mesh carbon-coated copper grid. The morphologies of the products were determined by scanning electron microscopy (SEM, FEI NanoLab 600i SEM/FIB dual beam system) and high-resolution transmission electron microscopy (HRTEM, JEOL 2011).

2.5. Magneto-transport measurements

Transport measurements was performed on individual Bi nanoribbons. As synthesized nanoribbons were dispersed on a silicon substrate firstly and then transferred into FEI NanoLab 600i SEM/FIB dual beam system, then four platinum (Pt) strips were deposited as the contact electrodes. The magneto-transport measurements were performed by a physical property measurement system (PPMS, Quantum Design Inc.) equipped with a 16 T superconducting magnet.

3. Result and discussion

By selecting two commonly used Bi sources and adjusting concentration in autoclave shown in Fig. 1 (a), solvothermal synthesis of nanostructured Bi samples were performed. It was found that the morphology and size of products were strongly dependent on the Bi ion source and concentration, affected slightly by the reaction conditions which were hence fixed at the mild and optimal parameters (at 200 °C for 24 h). As shown in Fig. 1 (b), nanospheres with the diameter range of 380 nm–1 μm and 2 μm particles with hexahedral shape were synthesized, by using $Bi(NO_3)_3 \cdot 5H_2O$ as the Bi ion source. No nanowire and nanoribbon were obtained, even when we timely adjusted the reaction parameters. Fortunately, when we changed the Bi ion source to $NaBiO_3 \cdot 2H_2O$, a small quantity of nanowires or nanoribbons were successfully synthesized, as shown in Fig. 1c. Although most of the samples were still nanospheres in the diameter range of 50–300 nm, these results illuminated the feasibility of Bi 1-2D structure synthesis, by using this novel, simple and low-cost solvothermal method in mild conditions and without a surfactant addition.

Since the characteristics of solvothermal synthesis samples comprising size, shape distribution, and crystallinity were proved to be altered by changing certain experimental parameters [23], we further adjusted the concentration of $NaBiO_3$ (C) with fixed reaction temperature, time and solvent type. It was interesting that the C seriously affected the dimension and percentage of synthesized nanoribbons. As shown in Fig. 2a, the SEM image indicates that when we double the amount of $NaBiO_3$, the number of nanowires and nanoribbons increases and the length increases up to 20 μm. In