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# Synthesis and Characterization of Bismuth Single-Crystalline Nanowires and Nanospheres

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A facile solution-phase process has been demonstrated for the selective preparation of single-crystalline bismuth nanowires and nanospheres by reducing sodium bismuthate with ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP) or acetone. Bismuth nanobelts and $Bi/Bi_2O_3$ nanocables could be also obtained by changing some reaction parameters. Various techniques such as XRD, EDXA, SEM, TEM, HRTEM, and FT-IR have been used to investigate the physical characteristics of these low-dimensional bismuth nanostructures.

## Introduction

One-dimensional (1D) nanostructures (such as wires, rods, and tubes) have attracted extensive interest in recent years due to their potential use as interconnects and nanoscale electronic, optoelectronic, and sensing devices.[1] Considerable effort has been devoted to the bulk synthesis of semiconductor and metal nanowires.[2,3] Bismuth, as a semimetal with a very small band gap, provides a very attractive model system for studying low-dimensional physical phenomena due to its highly anisotropic Fermi surface, low carrier densities, small carrier effective masses, and long carrier mean free path.[4] Theoretical model and experiments results indicate a semimetal−semiconductor transition in bismuth nanowires when the wire diameter is decreased to a certain value (about 50 nm).[5] Bismuth nanowire is also an attractive material for thermoelectric applications.[6]

However, few methods have been reported for the preparation of bismuth nanowires until now. An effect method has been employed to producing Bi nanowires with diameters in the range 7−200 nm by pressure injection of Bi liquid melt, or by infiltration and condensation of Bi vapor into the nanochannels of an anodic alumina template.[7] Electrochemical deposition has also been used to fabricate polycrystalline Bi nanowires, by plating materials of interest into a template of nanometer-sized pores created by nuclear particle track etching in polycarbonate membranes.[3a,8] So far, bismuth nanowires with diameters ranging from 30 to 200 nm were extruded from the surfaces of freshly grown composite thin films consisting of Bi and chrome-nitride owing to the high compressive stress in these films.[9] Recently, a hydrothermal process has been demonstrated by

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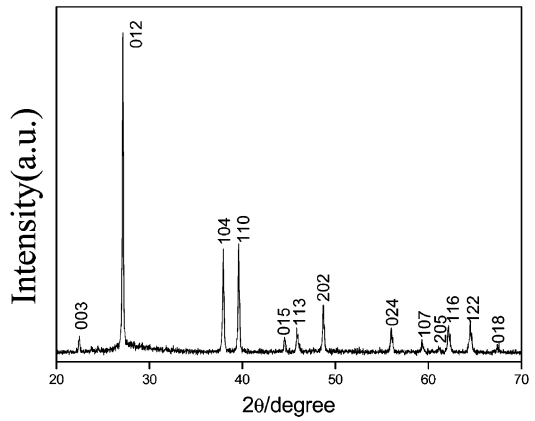


**Figure 1.** XRD pattern of as-synthesized bismuth nanowires.

us, for preparing single-crystalline Bi nanotubes.[10] A solvothermal process was also used to synthesize Bi nanowires from bismuth nitrite in ethylene diamene; however, this produced nanowires were with polycrystalline domain structures and low aspect ratios.[11] Here, we develop a template-free, solution-phase method for the production of single-crystalline Bi nanowires in large scale by reducing sodium bismuthate with ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP). This low-temperature synthetic route requires no physical templates or catalysts, and could be scaled up to produce bismuth nanowires without post-synthesis treatment for selective removal of templates or catalysts.

## Experimental Section

**Synthesis.** In a typical process, 0.15 g of analytical grade sodium bismuthate ($NaBiO_32H_2O$) and 35 mL of ethylene glycol or glycerol were put into a Teflon-lined stainless steel autoclave with a capacity of 50 mL at room temperature. The solution was then stirred vigorously and bubbled with a flow of pure argon gas for 30 min, before the autoclave was sealed and maintained at 180−200 °C for over 24 h. In different cases, PVP (MW ≈ 1 300 000), acetone, or water was introduced to control the morphology of the product. After the reaction was completed, the resulting black solid product was collected by filtration, washed with large amount of absolute ethanol and acetone to remove all of impurities, and then dried at 50 °C for 1 h.

**Characterization.** The X-ray diffraction (XRD) pattern was recorded on a powder sample using a Bruker advance-D8 diffractometer with Cu Kα radiation. SEM measurements were carried out with a LEO-1530 microscope, and TEM characterization was performed with a Hitachi-800 microscope. HRTEM and electron diffraction studies were obtained with a JEOL-2010 microscope. FT-IR spectrum was recorded on a Nicolet model 759 Fourier transform infrared spectrometer at wavenumbers 500−4000 $cm^{-1}$.

## Results and Discussion

**Composition of the Products.** On the basis of the above solution-phase process, pure Bi could be obtained. Figure 1 shows an X-ray diffraction (XRD) pattern of as-synthesized powders, and all the diffraction peaks could be readily indexed to the rhombohedral phase of bismuth. The lattice constants calculated from the XRD pattern were $a = 4.54$ Å and $c = 11.85$ Å, which were very close to the reported data (JCPDS 05-0519).

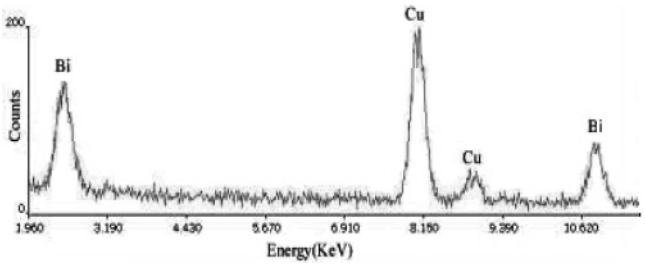


**Figure 2.** EDXA spectrum of a single bismuth nanowire.

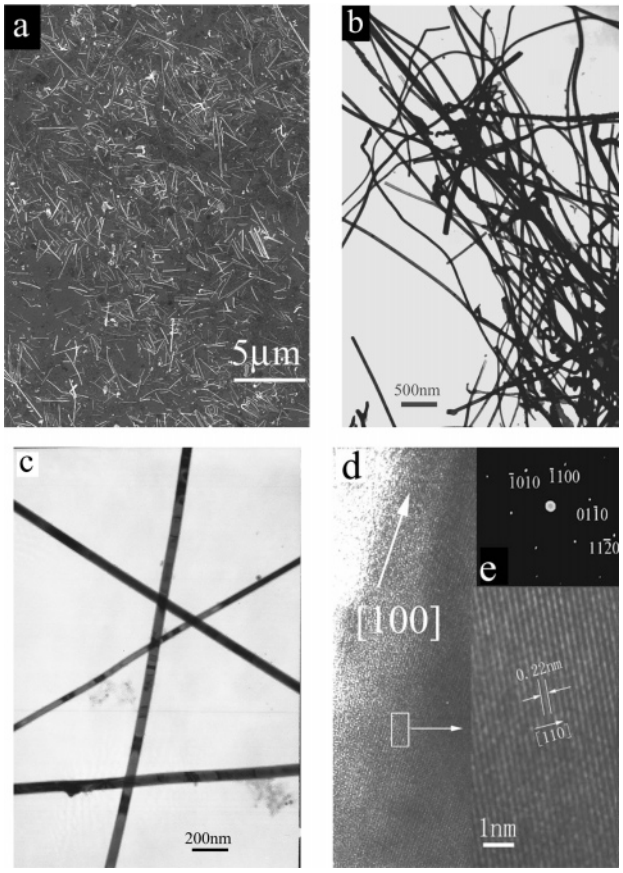


**Figure 3.** (a) SEM and (b, c) TEM images of bismuth nanowires that were synthesized by the polyol process in the presence of PVP. (d) A HRTEM image of an individual Bi nanowire showing good ordering of the lattice planes. (e) The corresponding electron diffraction pattern along the [0001] zone axis.

Thorough elemental composition analysis of bismuth nanowires was performed by energy-disperse X-ray analysis (EDXA) and revealed that the nanowires contained only bismuth. Figure 2 shows a typical EDXA spectrum recorded on an individual Bi nanowire, whose peaks are assigned to bismuth only (the Cu peaks arise from the copper grid).

**Morphologies and Structures.** The morphology of the powders was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 3a shows a typical SEM image of bismuth prepared in ethylene glycol with PVP, revealing high-yield growth of

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nanowire materials with lengths up to several micrometers. Figure 3b shows a typical low-magnification TEM image in which Bi nanowires with diameters in the range 10−200 nm were displayed. Figure 3c shows the TEM image of several nanowires, indicating the straightness of these nanowires. High-resolution TEM reveals high-quality single-crystalline Bi nanowires prepared by this polyol process. Figure 3d shows a high-magnification TEM image of a single-crystalline Bi nanowire. The spacing of 0.22 nm between adjacent lattice planes corresponds to the distance between two (110) crystal planes (at 60 to the wire axis), indicating ⟨100⟩ as the growth direction for the Bi nanowires. The electron diffraction (ED) pattern (Figure 3e) is identified to be along the [0001] diffraction zone axis, which is in good agreement with the hexagonal structure of bismuth. The oxide layer on the wire surface can be observed in HRTEM images, as shown in Figure 3d, because bismuth could be easily oxidized.[7b] The newly prepared bismuth nanowires could be preserved in some organic solvent such as hexane in order to prevent the oxidation.

The polyol process has been, recently, exploited to synthesize silver nanowires by reducing silver nitrate with ethylene glycol in the presence of PVP.[12] In the current process, PVP was found to play an important role in the production of Bi nanowires. Although Bi nanowires could be also obtained in the absence of PVP, the product contained a mixture of nanowires and nanospheres in this case. When PVP was introduced into ethylene glycol, the nanospheres would be hardly seen in the product, and the range of the diameters of as-produced nanowires narrowed. That is to say, PVP could strongly enhance the growth rate of a special crystallographic facet of seeds (for example, [100] for Bi), and the anisotropic growth of Bi was achieved with the help of PVP.

In order to further understand the nature of PVP influencing the formation of Bi nanowires, acetone was selected for manipulating the crystal growth of Bi in contrast. Figure 4 shows typical SEM and TEM images of Bi nanostructures synthesized in mixed solvents of ethylene glycol and acetone at different ratios, which indicate monodisperse and highly crystalline Bi nanospheres with different diameters. When the volume ratio of acetone and ethylene glycol reached 1, Bi nanoshperes dominated in the final product. The controllable diameters of Bi nanospheres could be also achieved by simply changing the ratios between these two solvents. Apparently, the "dilute" role of acetone leading to isotropic growth of Bi crystals is very different with that of PVP in our synthesis. As a result, Bi nanowires and nanoshperes can be selectively prepared by adjusting the additive components in the system. Because the solution-based reaction is quite a complex process, the systematic work is worth deeply investigating. Various reaction conditions, such as temperature, monomer concentration, and capping molecules, can be used to monitor and manipulate the kinetics of crystals growth.[14,15] We verified here that the adsorbent activity on the surface of crystal seeds could influence the shape control of nanostructures. In the current process, the temperature was another factor affecting the growth of Bi nanowires or spheres. The temperature should not be less than 180 °C; otherwise, Bi nanowires or spheres could hardly be formed.

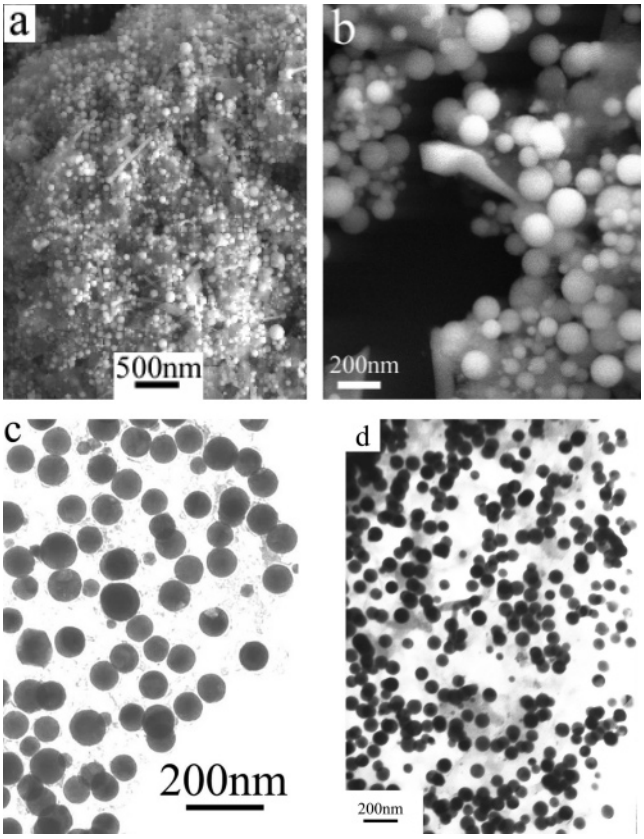


**Figure 4.** SEM (a, b) and TEM (c, d) images of Bi nanospheres synthesized in mixed solvents of ethylene glycol and acetone at ratios of 1:1, 2:1, 1:2, 1:4, respectively.

Other than Bi nanowires and nanospheres, we have also obtained some novel 1D nanostructures, such as Bi nanobelts and $Bi/Bi_2O_3$ nanocables, by changing some reaction parameters. If ethylene glycol was replaced by glycerol, the product would contain quite a few Bi nanobelts and nanospheres. Figure 5a shows a typical SEM image of Bi products obtained in glycerol, which contains Bi nanobelts and nanosphers. Figure 5b,c shows TEM images of structural uniform and single crystalline Bi nanobelts with a typical thickness in the range 20−50 nm and width 0.8−1.2 $\mu$m. The ED pattern (Figure 5b, inset) recorded on a single nanobelt is similar with that of Bi nanowires, which confirms the Bi structure of nanobelts.

Because bismuth is oxidizable, $Bi/Bi_2O_3$ nanocables could be obtained through a controllable oxidizing process in the presence of a trace of water. Figure 6 shows typical TEM images of $Bi/Bi_2O_3$ nanocables prepared in mixed solvents

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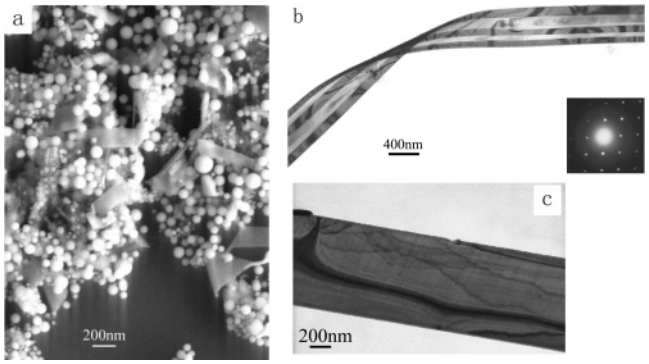


**Figure 5.** (a) SEM image of Bi products obtained in glycerol and (b, c) TEM images of an individual Bi nanobelt. The inset in b shows the corresponding ED pattern.

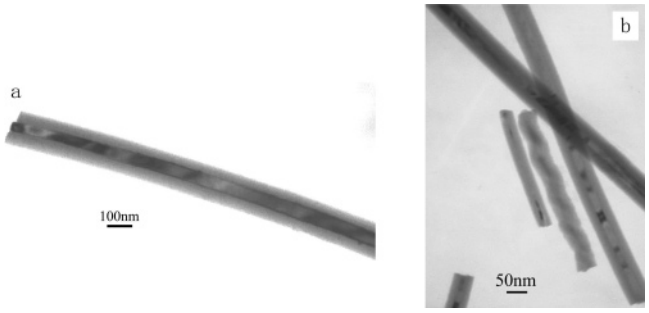


**Figure 6.** TEM images of $Bi/Bi_2O_3$ nanocables obtained through the polyol process in the presence of distilled water (5% volume ratio): (a) magnification TEM image of an individual nanocable, (b) TEM image of some $Bi/Bi_2O_3$ nanocables.

of ethylene glycol and distilled water (5% volume ratio) with PVP. Figure 6a shows a high-magnification TEM image of an individual nanocable, indicating clearly the crystalline Bi core and oxide shell. A variety of different 1D nanostructures, such as nanowires, nanobelts, and nanocables, will provide an opportunity to study the electronic properties of semimetal bismuth.

**Mechanism for the Formation of Bismuth Nanowires and Nanospheres.** The reproducible process involved the reduction of sodium bismuthate with ethylene glycol at 180 °C. In this so-called polyol process, ethylene glycol served as both solvent and reducing agent.[13] We selected sodium bismuthate as another reactant for its strong oxidation capability (the electric potential for $NaBiO_3/Bi$ is above 0.9 V). The chemical reaction can be formulated as

$$HOCH_2 - CH_2OH \rightarrow CH_3CHO + H_2O \quad (1)$$

$$5CH_3CHO + 2NaBiO_3 \rightarrow 2CH_3COONa + 3CH_3COOH + 2Bi + H_2O \quad (2)$$

The formation of Bi nanowires or nanospheres is believed to be based on the Ostwald ripening process.[14] At first, Bi nanoparticles were formed in the solution according to eqs 1 and 2. Some of these nanoparticles were able to grow into large crystals, which could serve as the seeds to grow into nanowires or nanospheres as the small ones were continuously dissolved. Figure 7a shows a U-type bismuth nanowire produced through this polyol process, which indicates that nanoparticles continuously grow into nanowires. According

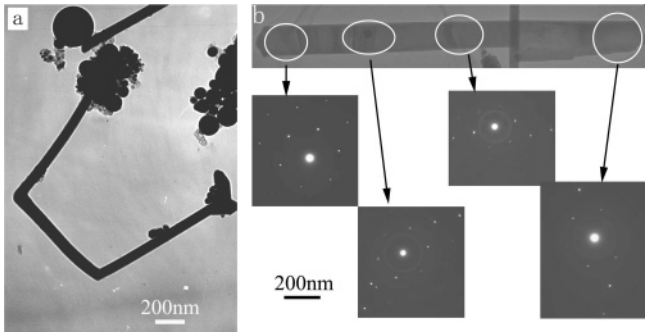


**Figure 7.** (a) TEM image of a U-type bismuth nanowire, and (b) ED patterns taken from different areas along with a single bismuth nanowire. These images show the formation of bismuth nanowires from nanoparticles.

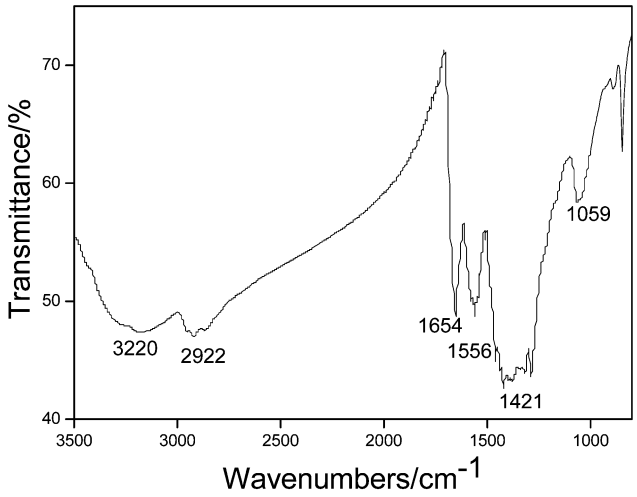


**Figure 8.** FT-IR spectrum of bismuth nanowires obtained in ethylene glycol with PVP.

to careful TEM studies, we found that the growth direction of some bismuth nanowires is not strictly consistent. Figure 7b shows a single bismuth nanowire and ED patterns taken from different areas along with this wire. These different ED patterns also reveal the formation of bismuth nanowires from nanoparticles.

Some recent research has indicated that the capping organic molecules in the reaction system could modulate the kinetics of the crystal growth and determine the subsequent morphology of the product.[12,15,16] For the current system, ethylene glycol or PVP molecules could adsorb onto the surface of Bi crystals through O−Bi bonding. The chemical adsorption between these organic molecules and bismuth nanocrystals could be proved by the FT-IR spectrum. Figure 8 shows a typical FT-IR spectrum of as-prepared bismuth nanowires in ethylene glycol with PVP. The sample was washed with absolute ethanol several times and then dried in a vacuum before used. The peaks could be assigned to PVP molecules adsorbed on bismuth nanowires,[17] but the C═O peak (1654 $cm^{-1}$) became weaker, which results from the interaction of O−Bi. Ethylene glycol or PVP molecules adsorbed on some surfaces of Bi nanocrystals could significantly decrease their growth rates and lead to highly anisotropic growth. Obviously, the interaction of PVP

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(17) http://www.chemexpert.com/.

molecules with the facets of Bi crystals is stronger than that of ethylene glycol. So, in the presence of PVP, a large amount of Bi nanowires in the product were obtained. As for Bi nanospheres, acetone should decrease the interaction between ethylene glycol and Bi nanoparticles, so the isotropic growth of Bi was subsequently realized.

## Conclusion

In summary, we have demonstrated a solution-phase approach to the large-scale synthesis of single-crystalline nanowires and monodisperse nanospheres of bismuth by reducing sodium bismuthate with ethylene glycol in the presence of PVP or acetone. The capping molecules in the reaction system have been found to play a key role in kinetically controlling the growth of bismuth nanowires. These nanowires could serve as templates to prepare some useful nanocomposites (for instance, $Bi/SiO_2$ nanocables). Bismuth and composite nanowires should exhibit excellent electronic and thermoelectric properties, and the measurement of these is currently underway.

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