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Facile synthesis and shape control of bismuth nanoflowers induced by surfactants

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ABSTRACT

Several nano-sized bismuth materials with different shapes were fabricated using ionic/nonionic surfactant as a synthesis agent. Ionic surfactants brought about the formation of irregular nanoparticles while nonionic surfactants directed the synthesis of uniform hexagonal nanoprisms. Among them, the nonionic surfactant Pluronic P123 (poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide), $PEO_{20}PPO_{70}PEO_{20}$) could act as the reductant/shape-directing bifunctional agent for successfully reducing Bi^{3+} to Bi^0 and inducing many hexagonal nanoprisms to grow from one crystal seed and finally form the graceful bismuth nanoflowers. The molding mechanism of bismuth nanoflowers might be attributed to the accommodation, stabilization and induction effects of P123 micelles for bismuth crystal seeds.

1. Introduction

Semimetallic bismuth is of many unique magnetoresistance and thermoelectronic properties: small effective mass, long mean free path of carriers, low density of states and highly anisotropic Fermi surface [1,2]. The distances between one bismuth atom and its three close neighbors in the same layer and the neighboring layers are 0.307 and 0.353 nm, respectively. The properties of bismuth particles depend strongly on their size and shape, which determine the surface structure of the particles. For example, bismuth undergoes a semimetal to semiconductor transition in nanowires the diameter of which is decreased to less than 50 nm [3]. It has been reported that bismuth nanowires exhibit an available thermoelectric figure of merit. Moreover, an enhanced thermoelectric effect might be achieved under more-restricted dimensionally conditions (e.g., nanocubes, nanoplates or nanobelts) [4].

Therefore, there has been increasing interests in two-dimensional bismuth nanomaterials, including nanowires, nanorods, nanosheets, etc., and their electronic or thermoelectric properties. Most of the previous researches have focused on the synthesis of two-dimensional bismuth nanowires using inorganic templates (e.g., porous Al_2O_3) [5] or polymer templates (e.g., polycarbonate membrane) [6]. However, it is difficult to obtain continuous and uniform structural bismuth nanowires. In addition, these methods are highly costly and complicated. Recently, some researchers tried to mass-produce two-dimensional bismuth nanomaterials by thermochemical methods. For example, the template-free synthesis approach based on a low-temperature reduction route has been developed for the fabrication of high-yield ultrathin bismuth nanosheets [7]. Besides, bismuth nanowires could grow on glass substrates using a radio frequency (RF) sputtering system [8]. Nevertheless, up to now, there are few reports on the high-effective synthesis of two-dimensional bismuth nanoprisms or nanoflowers materials, and it is difficult to balance the productivity and shape uniformity of the obtained bismuth nanomaterials.

In this Letter, we present a novel method to synthesize bismuth nanomaterial by using surfactants as reductant. Specifically, we found that the surfactants also play the role in controlling the shape of materials. By this method, different nano-structural bismuth materials were synthesized by using nonionic and ionic surfactants as shape-directing agent. Among the obtained bismuth nanomaterials, the nanoflowers were uniform and well crystallized. Therefore, the shape properties and molding mechanism of bismuth nanoflowers were investigated in the present Letter.

2. Materials and methods

2.1. Synthesis

At first, $Bi(NO_3)_3{\cdot}5H_2O$ (0.0064 g, ACROS chemical reagent) was added into 4 mL of 1.0 mol L^{-1} HNO_3 aqueous solution, and stirred at 30 °C until completely dissolved. The surfactants, including cetyltrimethylammonium bromide (CTAB, from Sinopharm, China), sodium dodecyl sulfate (SDS, from Sinopharm, China), triblock copolymers Pluronic P123 (poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide), $PEO_{20}PPO_{70}PEO_{20}$, from BASF, Germany), and F127 ($PEO_{100}PPO_{65}PEO_{100}$, from BASF, Germany) were

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dissolved in the water to obtain the 5 mmol L^{-1} surfactant aqueous solutions. Then 6 mL of surfactant aqueous solution was added to the $Bi(NO_3)_3$ solution with continued stirring by a magnetic agitator at 30 °C. The reaction took a few minutes to finish until some white precipitates appeared in the solution. These precipitates were centrifugalized (1000 rpm), collected, washed with ethanol, and air-dried at room temperature (30 ± 1 °C) before analysis.

2.2. Characterization

The samples were characterized by X-ray powder diffraction data (XRD), which were recorded on a Japan RigakuDmax-γA X-ray powder diffractometer with graphite monochromated Cu-Kα radiation (λ = 0.154178 nm). High-resolution scanning electron microscopic images, accompanied by energy-dispersive X-ray spectrum (EDS), were obtained with a field emission scanning electron microscope (FESEM S-4800, Hitachi, Japan), employing an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Effect of surfactant type

In the present Letter, we tried to employ four different surfactants acting as the reductant/shape-directing bifunctional agent. Triblock copolymers PluronicP123 and F127 are nonionic surfactants while CTAB and SDS are ionic surfactants. It has been suggested that the surfactant micelles might function as the shape-directing agent when the concentration of a surfactant reached the critical micelle concentration (CMC) [9]. Therefore, the high-concentration surfactant solution (5 mmol L^{-1}), much larger than the CMC of CTAB (0.89 mmol L^{-1}) [10], SDS (1.78 mmol L^{-1}) [11], P123 (0.05 mmol L^{-1}) [12] and F127 (0.55 mmol L^{-1}) [13], was used to induce the synthesis of bismuth nanomaterials. Figure 1 shows the SEM images of the as-prepared bismuth nanomaterials, which indicates that the type of surfactant plays a key role in the shape control of bismuth crystallites. As seen from Figure 1, ionic surfactants CTAB (Figure 1a) and SDS (Figure 1b) could not effectively direct the synthesis of bismuth crystals with regular shape, but bring abundant nanoparticles with a diameter of 20–40 nm. By contrast, the uniform bismuth crystals could be obtained in the presence of nonionic surfactants P123 (Figure 1c) and F127 (Figure 1d), and they are hexagonal nanoprisms with smooth surfaces. The productivity of bismuth nanoprisms induced by P123 was much higher than that by F127. Thus, we focused on adopting P123 as the reductant/shape-directing bifunctional agent to synthesize bismuth nanomaterials in the further researches.

3.2. Bismuth nanoflowers

In our Letter, P123 could be used to induce the formation of flower-like bismuth nanomaterials by optimizing the reaction conditions (increasing the reaction and washing time). As shown in Figure 2a, many clustered hexagonal nanoprisms, which grow up from a same seed crystal and stretch in all directions, compose the bismuth nanoflowers with the increase of the reaction time (compared with Figure 1c). The sizes of the 'petals' (nanoprisms) were 50–500 nm in diameter and 500–1000 nm in length, which became more uniform with the continuous increase of the reaction time (see Figure 2b). The washing process leads to the removal of the unreduced bismuth ions and unbound P123. The bismuth nanoflowers were 'soft' and easy to be holed by the electron beams during SEM observation (Figure 2c). The high-resolution microscopic image (Figure 2d) reveals that the petals were hexagonal prisms with cut angles. The inserted image at the upper-right corner also verified that the precursor of nanoprism was hexagonal, and the surface of nanoprism was smooth and uniform.

The element composition of the nanoflowers was analyzed through EDS. As seen from Figure 3a, the pure bismuth with a little of silicon substrate was detected, and no other element was found. Figure 3b shows the typical 2-theta XRD pattern of the bismuth nanoflowers. All diffraction peaks were indexed to the rhombohedral bismuth structure JCPDS No. 05–0519, R3m. Therefore, it can be affirmed that the Bi^{3+} was reduced to the Bi^0 in the aqueous solution, and then the Bi^0 crystallized into uniform shapes under the P123 directing.

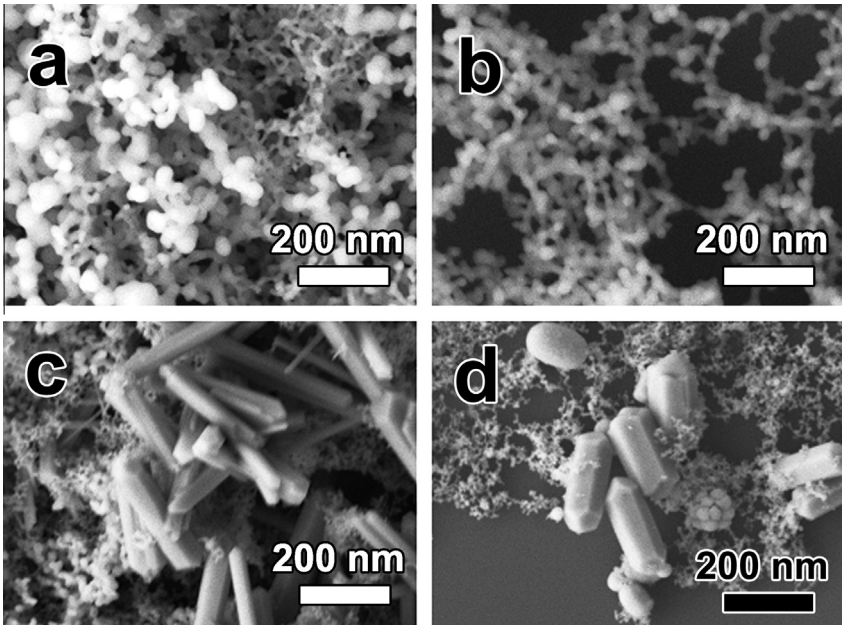

Figure 1. Scanning electron microscopic images of the as-prepared bismuth nanoparticles (a, b) and nanoprisms (c, d) obtained by using CTAB (a), SDS (b), P123 (c), and F127 (d) as reductant/shape-directing bifunctional agent (after 5 min).