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Letter

Microwave synthesis of bismuth nanospheres using bismuth citrate as a precursor

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ABSTRACT

Well-separated bismuth nanospheres were successfully synthesized from bismuth citrate and urea in diethylene glycol by a fast and simple microwave irradiation method. The products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In this fabrication, bismuth citrate plays a critical role as a precursor in the formation of bismuth nanospheres. The amount of urea also has an influence on the size of the bismuth nanospheres. The possible growth mechanism of bismuth nanospheres was discussed on the basis of the investigation of reaction time.

1. Introduction

Bismuth is a fascinating semimetal with unusual properties due to its highly anisotropic Fermi surface, low carrier densities, small carrier effective masses and long carrier mean free path [1]. Bismuth nanostructures have been extensively studied recently, since they play important roles in many diverse applications. For examples, single-crystal bismuth thin films exhibited large magnetoresistance and finite-size effects [2]. The thermal conductivity of single-crystal bismuth nanowire was found to be three to six times smaller than bulk materials [3]. Size-dependent transport and thermoelectric properties of individual poly-crystalline bismuth nanowires were also investigated [4]. Up to now, a wide variety of bismuth nanostructures have been synthesized, such as nanoparticles [5,6], nanowires [7], nanorods [8], nanotubes [9], triangular nanoplates [10], nanocubes [11] as well as nanospheres (>100 nm) [12–15]. Among the metal nanostructures, monodisperse metallic nanospheres have attracted considerable attention because of their unique optical, catalytic, novel chemical and biological properties [16–22]. For instance, spherical bismuth was a good catalyst for the growth of SnS_2 nanotubes and germanium nanowires [23,24]. Thus, much effort has been devoted to the preparation of metal nanospheres and their functional transformation [25–30]. Although many synthesis methods for bismuth nanospheres have been reported, there are still the problems of rigorous experimental conditions (under a stream of N_2) and long reaction time. Therefore, a simple, low-cost and rapid approach for the fabrication of bismuth nanospheres is highly desired.

In recent years, microwave irradiation method has received considerable attention as a new promising method for the one-pot synthesis of metallic and semiconductor nanostructures in solution [31–35]. Many metallic nanomaterials have been fabricated via microwave irradiation method [31,36]. In previous work, we described a simple refluxing method for the preparation of bismuth micro- and nanospheres from bismuth citrate and urea in the presence of PVP, using ethylene glycol as both solvent and reducing agent [13]. To the best of our knowledge, studies on synthesis of bismuth nanospheres by microwave irradiation have never been reported. In this communication, a rapid urea-assisted microwave irradiation method for the synthesis of bismuth nanospheres was reported. In this synthesis, bismuth citrate was used as a bismuth precursor.

2. Experimental

2.1. Materials and preparation

All chemicals are analytical grade and used without further purification. In a typical synthesis, 0.299 g (0.75 mmol) of bismuth citrate (Bi(cit)) and 0.135 g (2.25 mmol) of urea were added to a round-bottom flask which contained 50 mL of diethylene glycol (DEG). The mixture was stirred and sonicated until all the chemicals were well dispersed. Then the mixed solution was treated under microwave

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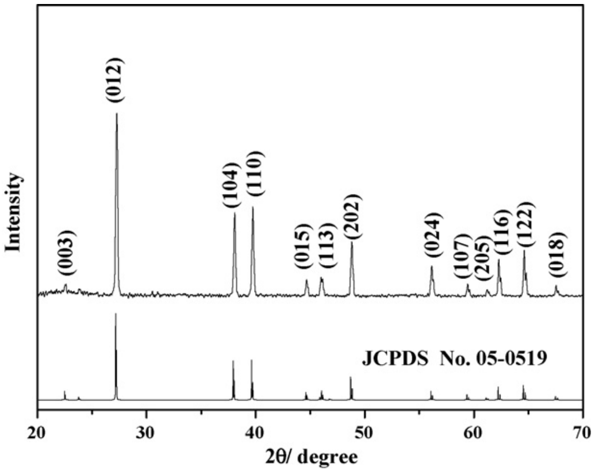

Fig. 1. XRD pattern of as-synthesized bismuth nanospheres with urea/Bi(cit) molar ratio of 3:1 under microwave heating for 20 min.

heating for 20 min with continuous vigorous stirring. After cooling down to room temperature naturally, the obtained black product was centrifuged and washed with deionized water for four times. Finally, the black product was dried in a desiccator for a few days for further characterization. Other samples were prepared under identical experiment conditions by using different bismuth precursors or different urea/Bi(cit) molar ratios.

2.2. Characterization

The obtained products were characterized by X-ray diffraction (XRD) (Bruker D8 advance), scanning electron microscope (SEM) (JEOL 6700-F), and transmission electron microscope (TEM) (Tecnai G2 20) with an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the typical powder X-ray diffraction (XRD) pattern of the as-synthesized product after 20 min microwave heating. All the diffraction peaks could be readily indexed to be rhombohedral phase of bismuth, which were consistent with the standard data (JCPDS No. 05-0519). No impurity was detected in the pattern, indicating that the product has high purity under current synthetic conditions.

The nanostructures of the products were examined by scanning electron microscopy (SEM). Fig. 2 displays the typical SEM images of the as-synthesized bismuth nanospheres at different time. As shown in Fig. 2a, only after 5 min microwave heating, spheric morphology of bismuth nanomaterials were observed in the sample. The diameters of these nanospheres varied from 40 to 500 nm. In this stage, bismuth nanosheets with diameters of about 500 nm were also formed. More and more bismuth nanospheres were fabricated with the increase of reaction time. It was observed that large quantities bismuth nanospheres were obtained (nearly 100%) when the reaction time was prolonged to 20 min (Fig. 2b). These nanospheres were well separated and the diameters of most nanospheres varied from 400 to 700 nm. Controlled experiments over different reaction time demonstrated the shape evolution and the corresponding growth process of bismuth nanospheres. Fig. 2c and d shows the SEM images of the dispersed bismuth nanospheres after 30 and 40 min microwave heating, respectively. It was found that the diameter of the nanospheres changed with the increase of reaction time. When the reaction time reached to 40 min, the maximal diameter of these nanospheres was about 1 μm, and the diameters of most nanospheres were more than 700 nm (Fig. 2d). The results indicate that reaction time plays an important role in the fabrication of bismuth nanospheres. Long reaction time does not favor the formation of small sizes of bismuth nanospheres. When the reaction time was prolonged to 30 min, the maximal diameter of some spheres was already at micrometer scale.

In this synthesis, it was considered that DEG was used both as solvent and reducing agent. In the initial step, the reaction mixture changed to black color after 3 min, microwave heating, which suggested the reduction of Bi^{3+} ions to bismuth by DEG in the solution. The reduction reaction of DEG might be similar to that of EG reported previously [37]:

$$2HOCH_2CH_2OCH_2CH_2OH \xrightarrow{\Delta} 2CH_3CH_2OCH_2CHO + 2H_2O \quad (1)$$

$$6CH_3CH_2OCH_2CHO + 2Bi^{3+} \xrightarrow{\Delta} 3CH_3CH_2OCH_2COCOCH_2OCH_2CH_3 + 2Bi + 6H^+ \quad (2)$$

There are many reports concerning the formation mechanism of inorganic nanospheres [38,39]. Generally, the formation of

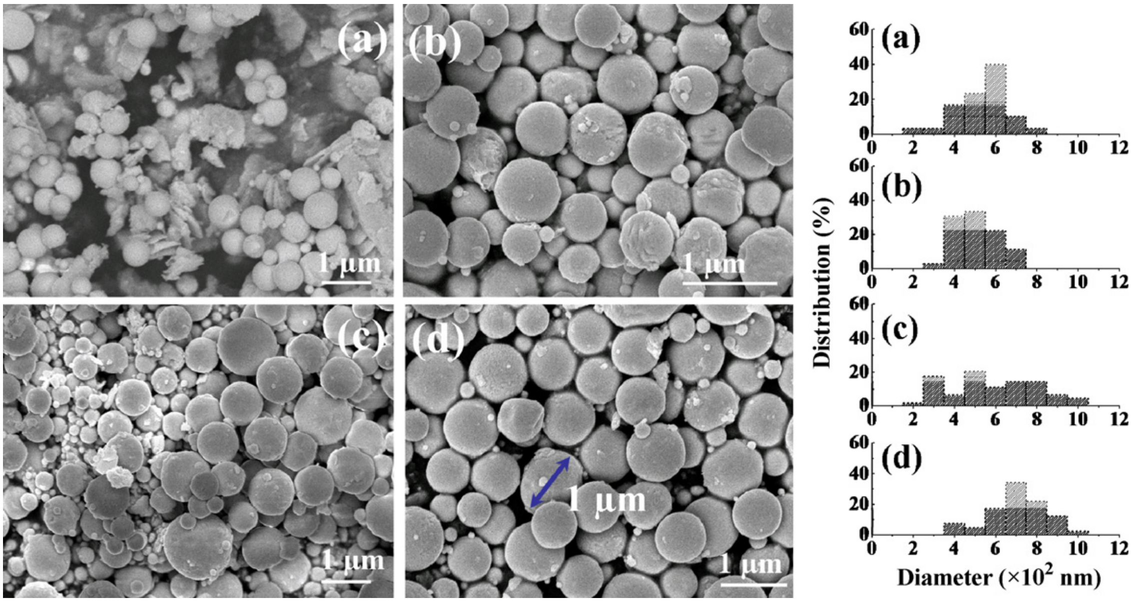

Fig. 2. SEM images and size distributions estimated from the photographs of the products synthesis by the microwave heating method with urea/Bi(cit) molar ratio of 3:1 for different time: (a) 5 min, (b) 20 min, (c) 30 min and (d) 40 min.

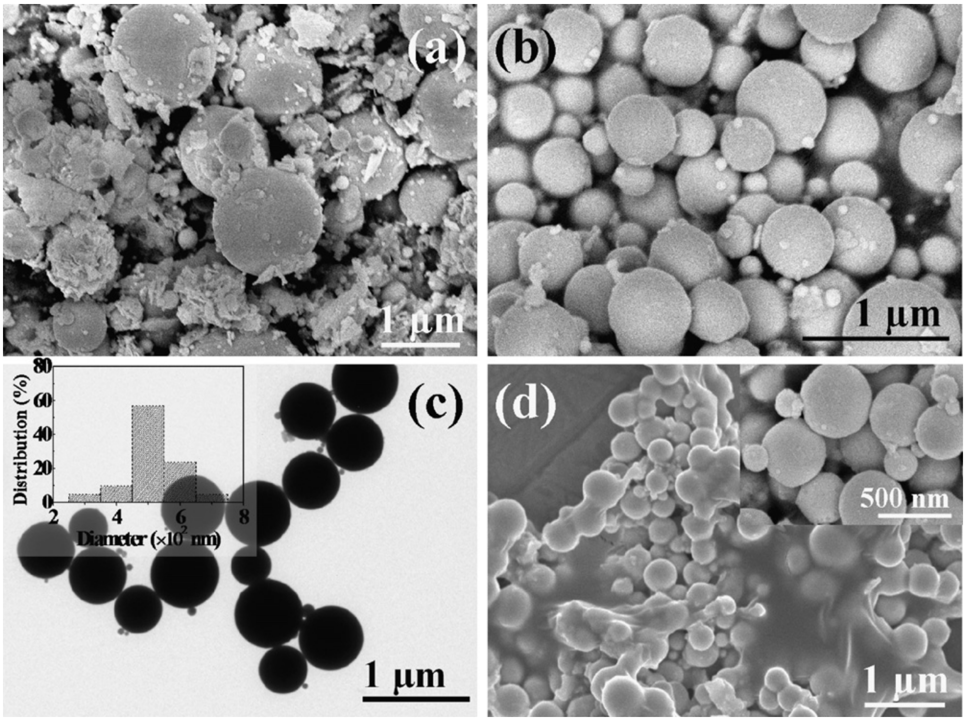

Fig. 3. SEM images of products sampled with different urea/Bi(cit) molar ratio for 20 min microwave heating: (a) 0, (b) 6 and (d) 9. *Note*: (c) shows the TEM images and size distributions (inset of "c") of the nanospheres corresponding to "b".

nanostructure features after fast nucleation in solution involved in two primary mechanisms: the aggregation growth process and the Ostwald ripening process [40,41]. Crystal growth by aggregation can occur by two means: random aggregation and the oriented attachment mechanism, which provide routes for the incorporation of defects in stress-free and initially defect-free nanocrystalline materials [42–44]. The Ostwald ripening process refers to the growth of larger crystals at the expense of smaller crystals, and this mode may result in the formation of faceted particles if the difference of surface energy sufficiently existed in different crystallographic facets [39,45]. In the present work, it was proposed that both of the two mechanisms were involved in the formation of bismuth nanospheres. First, DEG reduced Bi^{3+} ions to bismuth nuclei in the solution. The quick aggregation of bismuth nuclei led to the formation of bismuth nanosheets and nanospheres in this early stage (Fig. 2b), which is in agreement with random aggregation growth process. With the proceeding of microwave irradiation, the primary building units will dissolve in the solvent gradually and reprecipitate onto the larger nanocrystals, resulting in increasing the size of the nanospheres. The preferential growth into large crystals is determined by the oriented attachment and Ostwald ripening process.

The influence of precursors on the formation of bismuth nanospheres was investigated by altering the urea/Bi(cit) molar ratio. Fig. 3a shows the SEM image of the product prepared in the absence of urea. It was found that bismuth microspheres were formed, and irregular morphologies of bismuth nanomaterials were also observed. When the urea/Bi(cit) molar ratio was increased to 6, well-separated bismuth spherical particles with diameter distribution ranging from *ca.* 100 to 600 nm were fabricated, as shown in Fig. 3b and c. When the urea/Bi(cit) molar ratio was 9, the diameters of bismuth nanospheres were in range of 100–400 nm, which had a relatively narrow size distribution. However, the SEM image (Fig. 4d) shows that the nanospheres linked by the transparent films due to the excessive urea, which can be washed off by deionized water for more than four times (inset of Fig. 3d). The results illustrate that there is obvious difference of bismuth nanospheres diameters with the increase of urea concentration. Otherwise, the viscosity of the reaction system increased with the increase of the concentration of urea, which

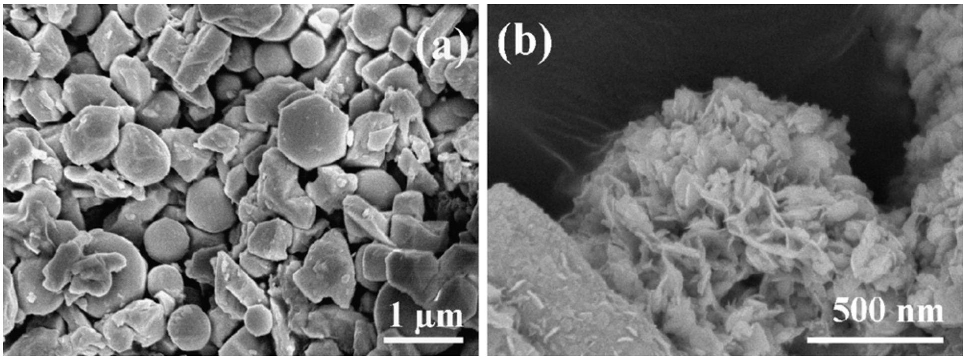

Fig. 4. SEM images of the products synthesis by the microwave heating method with urea/Bi-salt molar ratio of 3:1 using different bismuth precursors: (a) $Bi(NO_3)_3{\cdot}5H_2O$ and (b) $BiCl_3$.

made it difficult to remove the excessive urea under normal condition. It illustrates that the concentration of urea plays a key role in the size control of bismuth nanospheres, similar with the example of poly(vinylpyrrolidone) (PVP) capped bismuth nanospheres [13,14].

To further investigate the function of bismuth citrate, different bismuth precursors were introduced to the synthesis of bismuth nanospheres. When the urea/Bi-salt molar ratio was kept at 3, $Bi(NO_3)_3 \cdot 5H_2O$ and $BiCl_3$ was used as bismuth precursor under identical conditions, respectively, instead of bismuth citrate. As shown in Fig. 4a, bismuth nanospheres and irregular shapes of bismuth nanomaterials were obtained by using $Bi(NO_3)_3 \cdot 5H_2O$ as bismuth precursor. Interestingly, bismuth nanoflowers were fabricated when $BiCl_3$ was instead of bismuth citrate (Fig. 4b). It illustrates that the anions of bismuth salts have a great influence on the morphologies of growing bismuth nanostructures. In fact, citrate anion has been widely used as an effective capping agent to modify crystalline surface [46]. As shown in Fig. 3a, bismuth micro- and nanospheres were also obtained from bismuth citrate in the absence of urea. In this fabrication, citrate anions could generate from bismuth citrate during the reduction process. Citrate anion was not only an efficient capping agent but also exerted a significant function on the morphology of the growing bismuth nanoparticles [47].

4. Conclusions

In summary, we have developed, for the first time, a fast and economical route based on an efficient microwave assisted process for the preparation of bismuth nanospheres at large scale. The diameter of bismuth nanospheres was varied by altering the concentration of urea or the reaction time. Bismuth citrate plays a key role in the formation of bismuth nanospheres. This method here provided a more convenient, fast and economic way for the mass production of metal nanospheres.

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