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Tutorial

In situ investigation of bismuth nanoparticles formation by transmission electron microscope

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ABSTRACT

Bismuth (Bi) nanoparticles are prepared by using $NaBi(MoO_4)_2$ nanosheets in the beam of electrons emitted by transmission electron microscope. The formation and growth of Bi nanoparticles are investigated in situ. The sizes of Bi nanoparticles are confined within the range of 6–10 nm by controlling irradiation time. It is also observed that once the diameter of nanoparticles is larger than 10 nm, the Bi particles are stable as a result of the immobility of large nanoparticles. In addition, some nanoparticles on the edges form nanorods, which are explained as the result of a coalescence process, if the irradiation period is longer than 10 min. The in situ research on Bi nanoparticles facilitates in-depth investigations of the physicochemical behavior and provides more potential applications in various fields such as sensors, catalysts and optical devices.

1. Introduction

Recently, noble metal nanoparticles have attracted huge interest from scientific researchers owing to their unique and versatile properties (Longo et al., 2013; Murphy et al., 2008; Xia et al., 2009). For instance, silver nanoparticles have been widely used as materials for microelectronics, photoelectron, electronic conduction and catalysts due to their unique electrical, magnetic and antibacterial properties (Tsuda et al., 2012). Bismuth (Bi) nanoparticles, another popular noble metal nanoparticles, are referred as one of the most potentials for magnetic sensors (Yang et al., 1999) and thermoelectric devices (Wang et al., 2005b), since they have anisotropic Fermi surface, low carrier density and small carrier effective mass (Kim et al., 2007; Lin et al., 2000). Consequently, the design and preparation of noble metal nanoparticles have received enormous attention. Many novel methods are rapidly developed to meet facile preparation, including electrochemical deposition (Khaydarov et al., 2009), polymer-protected reduction (Yonezawa et al., 2001), microemulsion (Shah et al., 2000), hydrothermal methods (Li and Zhang, 2010; Lin et al., 2017; Shah et al., 2000; Wang et al., 2005a) and electron beam irradiation method (Pattabi et al., 2010). Among them, electron beam irradiation has been widely accepted for preparing noble and transition metal nanoparticles recently. The Kim group used an electron beam in a transmission electron microscope (TEM) to prepare highly monodisperse gold nanoparticles with an average diameter of 2.0 nm from Au(I)–SC polymer (Kim et al., 2005). Bi nanoparticles with a rhombohedral structure at an average diameter of 6 nm were synthesized by electron beam in TEM from sodium bismuthate (Sepulveda-Guzman et al., 2007). Pattabi et al. (2010) also synthesized silver nanoparticles with enhanced antibacterial activity by similar method. Bohler et al. (2013) reviewed low-energy, electron-initiated molecular syntheses and their applications in the modification of surfaces with metal nanoparticles. As is well established, addition to investigating morphologies, structures and chemical transformations (El-Atwani et al., 2015; San-Miguel et al., 2016), TEM can also be used to fabricate unique highly dispersed nanomaterials by electron beam irradiation.

Bi is a semimetal with small band overlap and it is an anisotropic electron effective mass-tensor. Nanostructures of Bi have been studied extensively due to their magnetoresistance, optical and excellent thermoelectric properties, which differ from bulk materials (Carotenuto et al., 2009; Derrouiche et al., 2010; Singh and Karmakar, 2011; Wang et al., 2014). In this research, we present the real-time in situ formation and growth of Bi nanoparticles from $NaBi(MoO_4)_2$ nanosheets irradiated by electron beam in TEM. The size of single-crystalline Bi is effectively controlled within the range of 6–10 nm. This observation of Bi nanoparticles formation can provide an alternative approach for in-depth investigations of the relevant physicochemical behaviors, as well as boosting potential applications in sensors, catalysts and optical

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devices.

2. Experimental

Firstly, $NaBi(MoO_4)_2$ nanosheets were prepared by using the early reported methods (Lin et al., 2016; Xu et al., 2016). All the reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. In a typical synthesis process, 0.97 g (4 mmol) $Na_2MoO_4{\cdot}2H_2O$ was dissolved in 70 mL deionized water, and then 0.69 g (1 mmol) bismuth glycerolate ($Bi_2(OCH_2CHOHCH_2O)_3$) was dispersed in the solution in an ultrasonic processor (Liu et al., 2016). The mixture, transferred into a 100 mL Teflon-lined stainless steel autoclave, were heated to 170 °C and kept for 12 h. The autoclave was taken out and cooled naturally to room temperature. The $NaBi(MoO_4)_2$ nanosheets were produced and collected by centrifugation. They were washed several times with deionized water and dried at 80 °C for 12 h. The crystal structure and morphology of $NaBi(MoO_4)_2$ were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

A sample was obtained by dispersing the as-prepared $NaBi(MoO_4)_2$ nanosheets onto a carbon-coated copper grid. In situ Bi nanoparticles evolution was observed during the electron beam irradiation in TEM (JEM-200EX) equipped with energy-dispersive X-ray spectroscopy (EDS) at 200 kV. The observation was carried out under an accelerating voltage of 200 kV, at a column vacuum pressure of 10^{-5} Pa and a beam current density of 15 pA cm^{-2} for 0–20 min.

3. Results and discussion

Fig. 1 is the XRD pattern of as-prepared $NaBi(MoO_4)_2$. All of the diffraction peaks observed can be perfectly indexed to the tetragonal scheelite $NaBi(MoO_4)_2$ (PDF card 51–1508, JCPDS). No other crystal phase was detected within 2% of XRD detection limitation. Fig. 2 is the morphology of $NaBi(MoO_4)_2$ sample by using SEM. As shown, the $NaBi(MoO_4)_2$ sample is mainly comprised of nanosheets.

TEM is used to observe the morphology of prepared $NaBi(MoO_4)_2$ sample and the formation of Bi nanoparticles under electron beam irradiation. Fig. 3 shows the TEM images of $NaBi(MoO_4)_2$ sample in an electron beam irradiation for 0, 2, 4, 6, 8, 15 min. It can be seen that the Bi nanoparticles appear uniformly and grow up remarkably in the first 8 mins, and the average size is 6 nm. The Bi nanoparticles keep stability with extending irradiation time. This is due to the rapid motion of tiny Bi particles in the initial stage of irradiation, then the motion slows down when the particle size of Bi is larger than 6 nm. The finial size of spherical nanoparticles is confined within the range of 6–10 nm after 15 min irradiation. The size uniformity of the Bi nanoparticles is better than the reported by Sepulveda-Guzman et al. (2007), and this growth

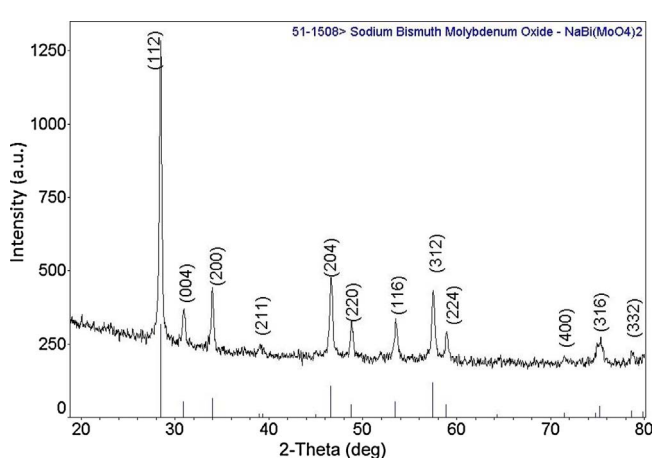

Fig. 1. XRD pattern of as-prepared $NaBi(MoO_4)_2$ nanosheets.

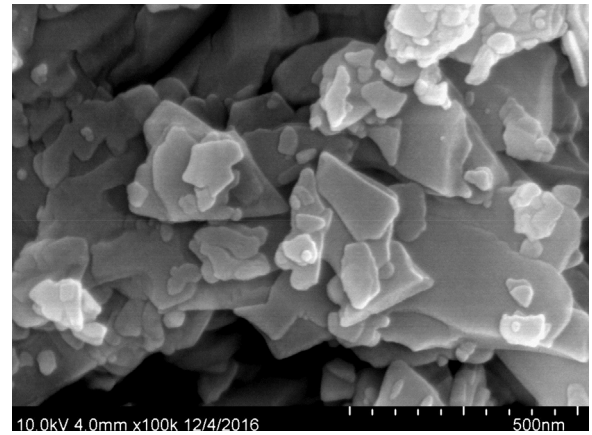

Fig. 2. SEM image of as-prepared $NaBi(MoO_4)_2$ nanosheets.

rate is slight higher than the rate (6 nm after 10 min) for Bi particles formed from $NaBiO_3$ irradiated by electrons under similar conditions.

In order to confirm the change in composition, the nanosheets and nanoparticles formed after electron beam irradiation are analyzed by using EDS. Fig. 4(a) shows the EDS spectrum of the prepared $NaBi(MoO_4)_2$ sample acquired at the beginning of the experiment. It exhibits peaks of Mo, Bi, Na, and O as well as peaks related to the carbon film and copper grid (C and Cu). Our semi-quantitative analysis is consistent with the atomic composition of $NaBi(MoO_4)_2$. Fig. 4(b) shows the EDS spectrum of an isolated Bi nanoparticle on the edge of nanosheet after electron beam irradiation for 15 min. The absence of Mo and Na peaks implies that the nanoparticle is mainly composed of Bi metal not $NaBi(MoO_4)_2$.

High-resolution TEM (HRTEM) images of $NaBi(MoO_4)_2$ and the formed Bi nanoparticles by electron beam irradiation are recorded in Fig. 5. Fast Fourier transform (FFT) is conducted on the images as inset. As shown in Fig. 5(a), the initial state of the $NaBi(MoO_4)_2$ nanosheet is single crystallite. The spots in the corresponding FFT are indexed to the (020) and (112) diffraction planes spacing of 0.268 nm and 0.316 nm, respectively. After irradiation for 4 min, four new spots arise among the original spots of $NaBi(MoO_4)_2$ in the FFT image, as observed in Fig. 5(b). This conforms the formation of Bi crystallite after the electron beam irradiation.

In Fig. 6(a), both Bi and $NaBi(MoO_4)_2$ phase zones are existed distinctly in the same HRTEM image. The corresponding FFT images are shown in Fig. 6(b) and Fig. 6(c), respectively. Fig. 6(b) shows the $[\bar{1}01]$ zone axis clearly, which is the spots of (000), (111), (010) and (101) derived from Bi nanoparticle (PDF card 51-0765, JCPDS). The other spots attributed to $NaBi(MoO_4)_2$ are also included in the FFT image. As a typical example, Fig. 6(c) indicates all the spots ascribed to (000), (112), $(1\bar{1}2)$ and (020) planes of $NaBi(MoO_4)_2$ nanosheet recorded from the $[20\bar{1}]$ zone axis.

According to the TEM images, the sizes of most Bi nanoparticles are less than 10 nm even though the irradiation time was extended. This is due to the reaction equilibrium of $NaBi(MoO_4)_2$ decomposition under electron beam irradiation and the immobility of larger nanoparticles. However, some of Bi nanoparticles on the edges of $NaBi(MoO_4)_2$ nanosheets grow into large crystals via coalescence process, as shown in Fig. 7. Unlike the Ostwald ripening process, which is mostly related to smaller nanoparticles and occurs during the early stage of irradiation (Sepulveda-Guzman et al., 2007), the coalescence involves the diffusion of an entire particle which collides with other particles. During the coalescence process, two nanoparticles of 6 nm connected at the end and then merge into one nanorod. This diffusion mechanism is most likely caused by continuous irradiation and weak interaction between the particles and the support depending upon several factors such as temperature, support substrate and electron beam intensity (Chen et al., 2006).