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Letter

Microemulsion-processed bismuth nanoparticles

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Abstract

Bismuth (Bi) is classic semi-metal with a low carrier density, small carrier effective masses, very long mean free path and highly anisotropic Fermi surface. In this work, we present a technique for the synthesis of bismuth nanometer-sized particles using an inverse microemulsion method. To prevent air-oxidation in the characterization stage, poly(vinylpyrrolidone) was used as protecting agent. Our characterizations reveal that single rhombohedral phase of bismuth can be obtained with ultrafine particle with ~20 nm in size by following this synthetic route. The optical absorption spectrum of the aqueous nanoparticle colloids shows an absorption band at ~268 nm.

Keywords: Bismuth; Microemulsion; Nanometer-sized particle

1. Introduction

The semimetal bismuth is an interesting material for electronics because of its highly anisotropic electronic behavior, low conduction-band effective mass and high electron mobility [1]. It has been reported that a conversion from a semimetal to a semiconductor could occur in thin Bi layer grown by molecular beam epitaxy [2]. This size-induced semimetal to semiconductor transition and related quantum confinement effect are potentially useful for certain optical and electro-optical device applications [3]. It has also been suggested that the nanoscale bismuth system is attractive as a potential thermoelectric material [4]. In order to prepare a thin layer of bismuth, a processing of nanometer-sized bismuth with narrow size-dispersity is necessary to be performed as the first step. Previously, we have successfully prepared nanometer-sized bismuth using an inverse microemulsion method coating with in-situ polymerization [5]. In this letter, the emphasis lies in a development of colloidal synthesis route in producing bare nanometer-sized bismuth particles. The particle morphology and optical property of as-prepared sample are discussed as well.

2. Experimental procedure

2.1. Chemicals

The starting materials used in this study include bismuth (III) citrate (>99.99% in purity), sodium borohydride (99.0% in purity), poly (oxyethylene)$_9$ nonyl phenol ether (hereafter NP9), polyvinylpyrrolidone (hereafter PVP, $M_w \approx 29\,000$), all above chemicals were from Aldrich, U.S.); petroleum ether (b.p. 60–80°C, from Fluka and packed in Switzerland), ammonia solution (concentration: 28.0–30.0 wt.%, GR solution from EM Science), and poly (oxyethylene)$_5$ nonyl phenol ether (hereafter NP5, from Albright and Wilson Asia Pte Ltd., Singapore). All the solvents were Ar-degassed before use.

2.2. Preparation of nanometer-sized bismuth powder

Surfactants NP5 and NP9 were pre-mixed in a weight ratio of 8:1. An inverse microemulsion system consist-

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ing of 60.30 wt.% petroleum ether, 28.20 wt.% mixed surfactant (NP5 + NP9) and 11.50 wt.% aqueous solution of 0.50 M $NaBH_4$ in 1.00 M $NH_3{\cdot}H_2O$ was subsequently established. Another ternary system containing 60.30 wt.% petroleum ether, 28.20 wt.% mixed surfactant (NP5 + NP9) and 11.50 wt.% aqueous solution of 0.10 M bismuth (III) citrate in 1.00 M $NH_3{\cdot}H_2O$ was simultaneously prepared as well. The Bi-containing system was then titrated at a rate of ~30 drops per minute into the microemulsion system while vigorously stirring. The resulting nano-bismuth powder was initially separated by a high-speed centrifugation, and was eventually retrieved by repeatedly washing away the oil and surfactant using ethanol, followed by centrifugal recovery and vacuum drying. All the above operations were performed under a nitrogen atmosphere in a glove box.

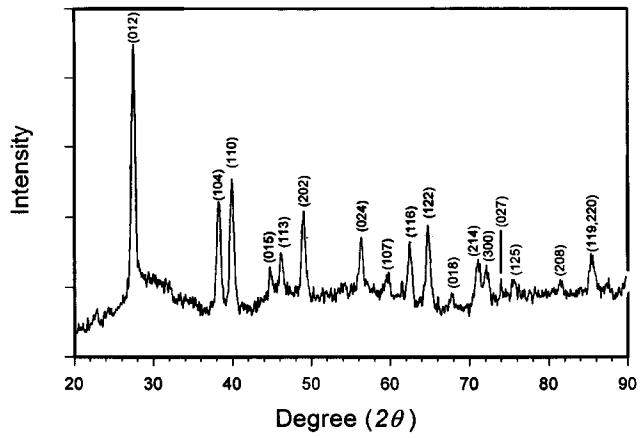

Fig. 1. XRD trace of the bismuth nanometer-sized particles prepared via the reverse microemulsion method.

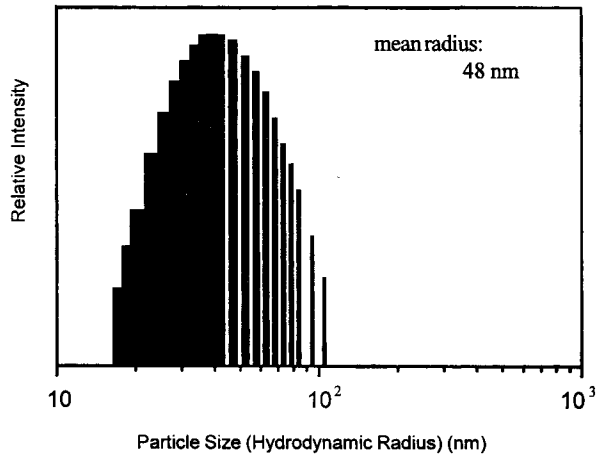

Fig. 2. Particle/aggromerate size distribution of bismuth powder derived via the microemulsion processing route.

2.3. Characterizations

The as-prepared bismuth powder was dispersed into distilled water in a capped quartz cell under nitrogen and its optical density was measured using a Cary UV–Vis spectrophotometer (Cary Varian Optical Spectroscopy Instruments). To minimize the degree of aggregation, the sample was mechanically re-dispersed using an ultrasonic source before the measurement. This bismuth colloidal 'solution' in a capped cell was also characterized for particle/agglomerate size distribution using laser scattering technique (DynaPro 99 Molecular Sizing Instrument). A drop of the resulting solution was dried onto a carbon coated TEM grid and a JEOL 2010 transmission electron microscope was employed to observe the particle morphology. Phase identification was performed at room temperature using a (CuK_α) X-ray differactometer (Philips X'pert Systems). To prevent the formation of oxides, bismuth sample for XRD measurement was coated with PVP ($M_w = 29\,000$) by re-dispersing the powder into a PVP solution in ethanol (Bismuth: PVP ≈1:1 in weight ratio) under nitrogen and vacuum drying.

3. Results and discussion

3.1. Phase identification

To identify bismuth nanoparticles prepared from the reverse microemulsion method, an XRD phase analysis was performed. The sample was pre-coated using PVP polymer to avoid an oxidation during the determination processing. Fig. 1 illustrates the XRD pattern of as-prepared bismuth, showing a highly crystallized rhombohedral bismuth phase. All the major peaks are labeled and attributed to the formation of rhombohedral bismuth according to the standard ICDD PDF (Card No. 05-0519). Crystalline size was determined by applying the Scherrer equation [6] to the line broading of the (012), (110) and (202) peaks, i.e.

$$D = 57.3 \times k\lambda/(\beta \cos\theta),$$

where k is particle shape factor (taken as 0.9), λ the wave length of $CuK_{\alpha 1}$ radiation (1.54056 Å), β the calibrated half intensity width of the selected diffraction peak (degrees), θ the Bragg angle (half of the peak position angle), D the crystallite size (Å), and the factor 57.3 is used to convert β in degree to radian measure. From this equation, the average size of bismuth crystallites of the sample was estimated to be ~13.3 nm.

3.2. Particle morphology

Fig. 2 is TEM micrograph further showing the morphology of as-prepared bismuth nanoparticles. To pre-

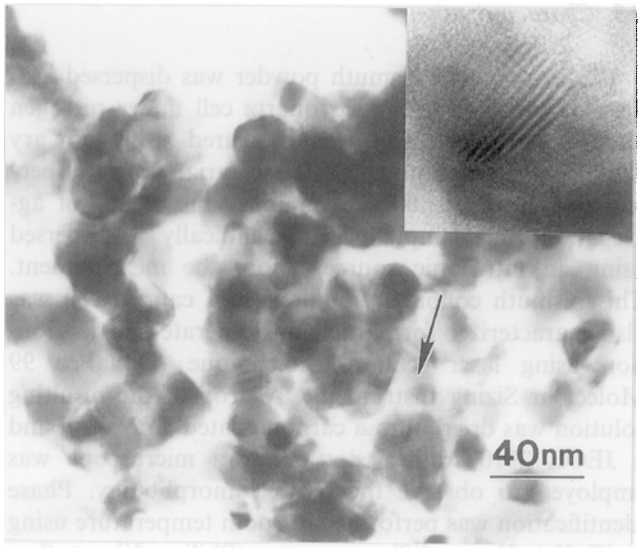

Fig. 3. Transmission electron micrograph of bismuth nanoparticles prepared via the reverse microemulsion method.

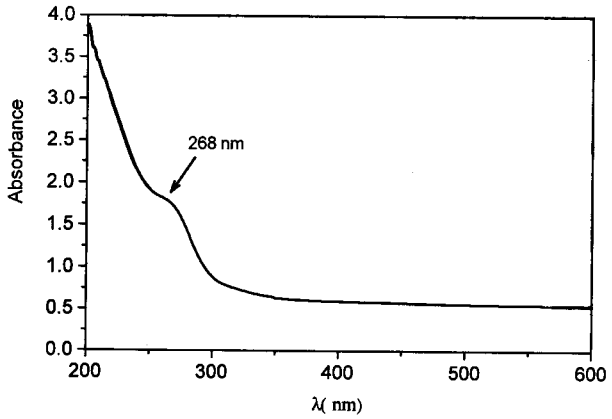

Fig. 4. Surface plasmon resonance of nanometer-sized bismuth in aquoeous solution.

vent air-oxidation, the sample dropped onto a carbon coated TEM grid was pre-coated by adding PVP–ethanol solution under nitrogen. This micrograph reveals that the bismuth particles formed in the presence of PVP prepared through this synthetic route are shaped spherically. The size of particles is in the range about 20 nm in diameter. Although the particle edges are ambiguous, which is probably due to the presence of polymer and polymer-caused aggregation of particles, a lattice image can still be clearly detected as shown in Fig. 2.

3.3. Size distribution

Fig. 3 shows a laser light scattering result of as-prepared bismuth powder in water, indicating the size distribution of particles. Sample was pre-dispersed in water and subsequently sealed in a special quartz cell. Fig. 3 demonstrates that the mean hydrodynamic radius of the sample is around 48 nm although the size distribution ranges between 18 and 105 nm in radius. As expected, the particle size measured by light scattering technique is larger than that measured either by TEM or by XRD due to the different instrumental nature of working function. Effect from solvent molecules certainly contributes to the apparent particle size in the light scattering measurement. Moreover, size of agglomerates is, most likely, involved in this investigation as well.

3.4. Optical absorption

Fig. 4 is an UV absorption spectrum showing the surface plasma resonance of nanometer-sized bismuth (without polymer) in water. It is believed that the residue of the surfactant(s) has been efficiently removed by repeatedly washing the colloidal particles before the powder was dried as described above. Having been mathematically subtracted the contribution from water from the spectrum, resolved curve reveals that the absorption peak is centered at $\sim$268 nm. M. Gutiérrez et al. [7] previously reported that nanometer-sized bismuth particles exhibited an absorption at $\sim$253 nm, supported by a γ-radiolysis of $BiOClO_4$ experiment. According to the calculation result done by Creighton et al. [8], the first absorption band of 10 nm bismuth particles should appear around 270–280 nm. Our result is between the above two literature values.

4. Conclusions

Nanometer-sized particles of bismuth have been synthesized by an inverse microemulsion method. X-ray diffraction data and TEM image indicate that a single rhombohedral phase of bismuth can be obtained with a nanometer-sized crystal structure. Laser light scattering technique subsequently reveals that the hydrodynamic radius of bismuth in water is about 48 nm in mean value. The surface plasma resonance of the nanoparticle colloids in water also shows an absorption band at $\sim$268 nm. In addition, the oxidation problem during the stage of subsequent characterization can be eliminated by using a PVP polymer technique. This also demonstrates a feasible route to produce single phase, air-sensitive metal nanocrystallites.

Acknowledgements

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