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Nanometer-sized Bismuth Crystallites Synthesized from a High-temperature Reducing System

Jiye Fang*, Kevin L. Stokes, Weilie L. Zhou, C. B. Murray† and Charles J. O'Connor
Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148
† IBM T. J. Watson Research Center, Yortown Heights, NY 10598

ABSTRACT

Nanometer-sized bismuth has successfully been prepared using a high-temperature organic reducing system by presence of proper capping/stabilizing agents. Self-assembly of bismuth was, at the first time, obtained using size-selected nanoparticles (15nm in size). Various synthetic conditions, which may significantly affect the formation of self-assembled nanocrystalline bismuth, have been optimized and discussed in this paper. The as-prepared nanocrystallites exist in a single rhombohedral phase with high crystallinity, and oxidation problem has been efficiently overcome within limited period by employing this method.

INTRODUCTION

The semimetal, bismuth, has been attracted more interests because of its low effective mass, highly anisotropic Fermi surface and the potential to induce a semimetal-semiconductor transition with decreasing crystallite size [1]. Recent theoretical studies suggest that bismuth materials of reduced dimensions may exhibit enhanced thermoelectric properties at room temperature [2]. Most previous work on low-dimensional bismuth has understandably focused on one-dimensional wires synthesized [3,4]. An alternative approach is to use chemically synthesized nanometer-sized particles to build an electrically conductive solid film. Previously, we presented a report in which bismuth nanoparticles were synthesized in reverse microemulsions and isolated as a powder as well as encapsulated within a polymer matrix [5]. Recently, E. E. Foos et. al. [6] published an achievement in synthesizing bismuth nanocrystallites again using reverse micelles by reducing an aqueous bismuth salt inside of the surfactant AOT (sodium dioctyl sulfosuccinate). Since the electrical connection between the particles requires producing a close-packed assembly of bismuth nanoparticles (2D), however, both of above efforts were still far from the electrical measurement stage due to the gap between particles isolated by either polymer or surfactant, which is difficult to be eliminated in certain range of temperature (the melting point of bulk bismuth is only 271 ^{o}C). It is, therefore, necessary to improve the methodology in processing bismuth particles. Another process, high-temperature reduction in non-polar organic solution, is an interesting method as it can offer a self-assembled collection of highly crystalline, nanometer-sized particles capped with an organic ligand that should be removable at a low heating temperature in the next measurement stage. Experimentally, this process has proven successful in producing high-quality nanoparticles and extended colloidal solids of II-VI semiconductors [7] and transition metals [8]. In this paper, we report, at the first time, our synthetic results on self-assembly of bismuth semimetal nanoparticles by reducing an organometallic bismuth salt with protection ligand at high temperature.

EXPERIMENT

The synthesis of bismuth nanocrystallites was carried out, in octyl ether (a non-polar solvent with high boiling point), using standard organometallic reaction procedures with airless/moisture-less devices and commercially available reagents. The starting materials used in the present investigation include bismuth 2-ethylhexanoate (Alfa Aesar, Cat. No. 36710), lithium triethylborohydride (super-hydride) (1.0M solution in tetrahydrofuran, Aldrich), octyl ether (99%, Aldrich), trioctylphosphine (TOP) (90%, Aldrich), Oleic acid (>99%, Alrich), hexane (anhydrous, >95%, Aldrich), ethanol (>99.5%, Aaper Alcohol & Chemical Co.). Super-hydride solution in octyl ether was freshly prepared by mixing the commercial super-hydride solution in tetrahydrofuran (THF) (1.0M) with double volume of octyl ether under atmosphere of an inert gas (Ar) and subsequently all THF was completely evaporated. The rest of the chemicals were used without further purification.

The particle size and size distribution of each size-selected sample in prepared bismuth colloidal solution was monitored using dynamic laser scattering (DynaPro 99 Molecular Sizing Instrument from Protein Solutions, Inc.). Sample was dispersed in hexane and transferred into a special capped cell under argon. A drop of sample in hexane was also dried onto a carbon coated TEM copper grid and a JEOL 2010 transmission electron microscope was employed to observe the morphology of individual particles and particle assembly. To prevent possible oxidation, TEM sample preparation and storage were conducted in a glovebox, and an argon-filled plastic bag was employed to transfer the sample to the electron microscope. Phase identification was performed at room temperature using (CuK_{α}) X-ray diffractometer (Philips X'pert Systems). The bismuth nanoparticles were prepared for XRD measurements by first depositing a hexane nanoparticle colloid solution onto silicon wafer (in an argon atmosphere) and dried. To prevent the formation of oxides, the resulting film was coated with a 2-propanol solution of PVP (M_w = 29, 000) and then vacuum-dried.

A typical experiment involved a total of about 25 ml of solution. The proper amount of bismuth 2-ethylhexanoate and oleic acid (in a molar ratio of 1:10) was dissolved in 20 ml of octyl ether. The temperature was raised to 100°C and TOP (molar ratio between TOP and oleic acid was fixed as 4:1) was injected into the solution with a syringe while stirring under flowing argon. The temperature was further increased up to the reaction temperature (normally 175°C). Reduction of bismuth took place by injecting 0.5 M LiBEt3H in octyl ether. The resulting black solution was maintained at this temperature for 5 min. under an argon stream to allow formation of bismuth nanocrystals. The flask was quickly taken into the glovebox and the mixture was subsequently cooled down to room temperature. Particles were precipitated by adding ethanol to the system and collected by centrifugation under argon atmosphere. The precipitate was then redispersed into hexane. Particle size selection of the original colloid was performed by titration of ethanol (a polar solvent) into the hexane colloid. Adding the ethanol caused the largest particles to flocculate, and this mixture can be separated by centrifugation. This fractionation was repeated to produce several size distributions.

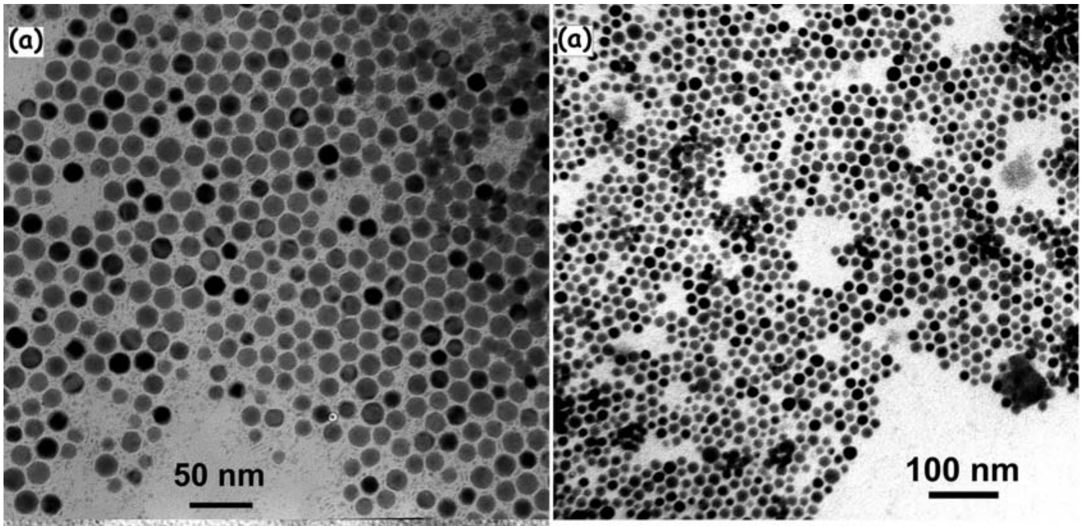
RESULTS AND DISCUSSION

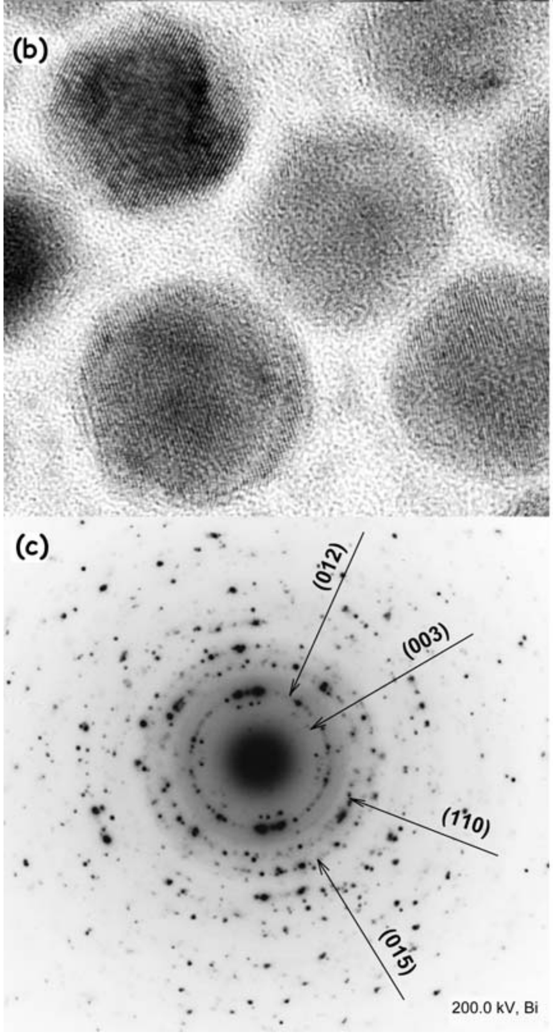
The formation of nanoparticles from a redox reaction in colloidal system is a very complicated process. The process begins with rapid nucleation and formation of small clusters followed by the slow coalescence of these initial clusters into larger particles. A variety of stabilizing/capping ligands, such as surfactants and polymers, have been employed to control particle growth, stabilize particle dispersions and limit oxidation of the particles [9]. The as-prepared collioids should be stable when a repulsive force of sufficient strength and range exists to counteract the combined sttractive forces. In our synthetic approach, TOP (trioctylphosphine) was used as a capping agent to limit the growth of particles. Oleic acid was also used as a stabilizing agent. It is generally accepted that TOP reversibly coordinates neutral metal surfaces sites, slowing but not stopping particle's growth; while oleic acid can assist TOP in stabilizing the system [8,10]. The capping ligand allows the particles to be dissolved and manipulated in nonpolar solvents and prevents agglomeration and oxidation of the particles. Another key point is to select a proper source of bismuth precursor. In this work, bismuth 2-ethylhexanoate, soluble in octyl ether as the high boiling point reaction medium, was used as the bismuth precursor. In addition, LiBEt3H (super-hydride) was used as the reducing agent. However, commercial LiBEt3H is supplied in a tetrahydrofuran (THF) solution. Since THF is a polar solvent, it must be completely removed and replaced by octyl ether under inert gas before use [8,10].

Figure 1 (a) (both small and large scale) shows a transmission electron micrograph (TEM) image of the bismuth particles after the 6th size-selection. The particles possess a spherical morphology with an average diameter of 15 ± 2 nm. The particles assemble into a near-2D monolayer with local hexagonal order. High resolution TEM image in Figure 1(b) shows fringes from the continuous lattice structure of a typical crystallite. The select electron diffraction pattern is shown in Figure 1(c), indicating that the bismuth particles possess high crystallinity and a single rhombohedral phase. The lattice plane distances calculated from the diffraction rings is consistent with those of rhombohedral (bulk) bismuth. The presence of single rhombohedral phase was confirmed by investigating the XRD patterns, which are shown in Figure 2 (a-c). From the as synthesized particles (coarse particles without size selection, Figure 2(a)) to 6th-size-refined ones (Figure 2(c)), all the bismuth samples exhibit rhombohedral phase. There was no trace of oxide phase determined. We have estimated the particle size for each sample from the x-ray diffraction (XRD) line broadening of the (012), (104) and (110) peaks using the Scherrer Equation [11]. In coarse particles, the average crystallite is by means of 33 nm in diameter. After the first size selection, the resulting colloid contains 23 nm (diameter) average particles. The 6th size-selected fraction contains 15 nm particles.

The average particle size and size distribution were estimated by using light scattering technique and from the TEM images by directly measuring the diameters of several hundred particles as well. Figure 3 (a,b) show the size histograms of the 6th size-selected fraction of particles, determined from both techniques. The particle diameter for the 6th size-selected fraction of particles is found to be 15 nm +/- 2 nm. It also reveals that self-assembly occurs only when the particle size tends to quasi-monodispersion. Comparison of the particle size determined from TEM to the particle size determined from XRD suggests that our particles our single-domain crystallites. It is worth mentioning that rhombohedral bismuth is the only detectable phase in both our TEM observation and XRD data.

Of the number of possible interactions among bismuth particles in the colloidal system, the most important things are the attractive van der Waals forces and the much shorter range steric repulsion provided by the tails of the organic ligands, which allows the nanoparticles to condense hexagonal-close packed mesoscopic crystal or amorphous structure. This type of ordered assembly is impossible from ionically stabilized colloids since the repulsive Coulomb interaction has a much longer range than the attractive van der Waals interaction between particles. To obtain a closed-packed assembly of nanoparticles and avoid aggregates, it is





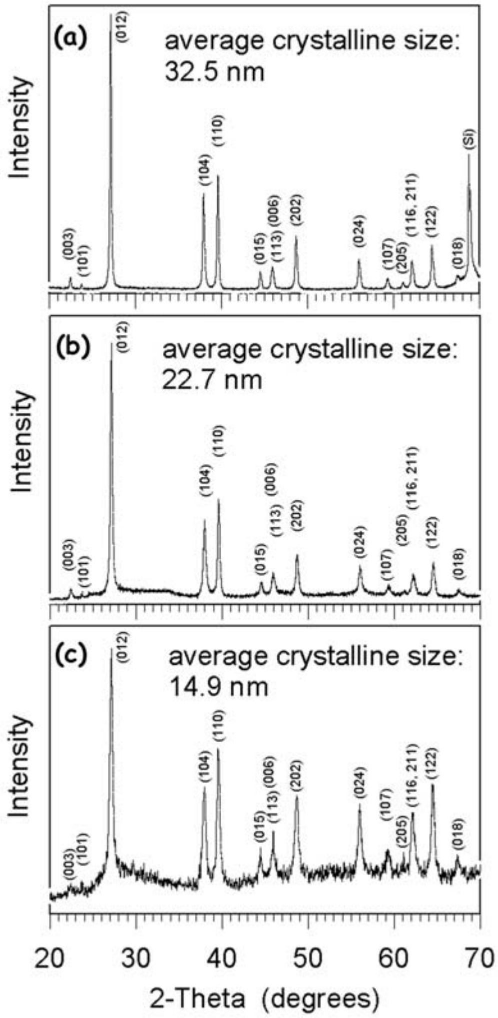


Figure 1. TEM images of bismuth nano-particles. (a) morphology of self-assembled bismuth particles after the 6th size-selection; (b) HRTEM of same sample; and (c) selected area electron diffraction pattern.

Figure 2. XRD of bismuth particles. (a) as-synthesized; (b) after the1st size-selection; and (c) after the 6th size-selection.

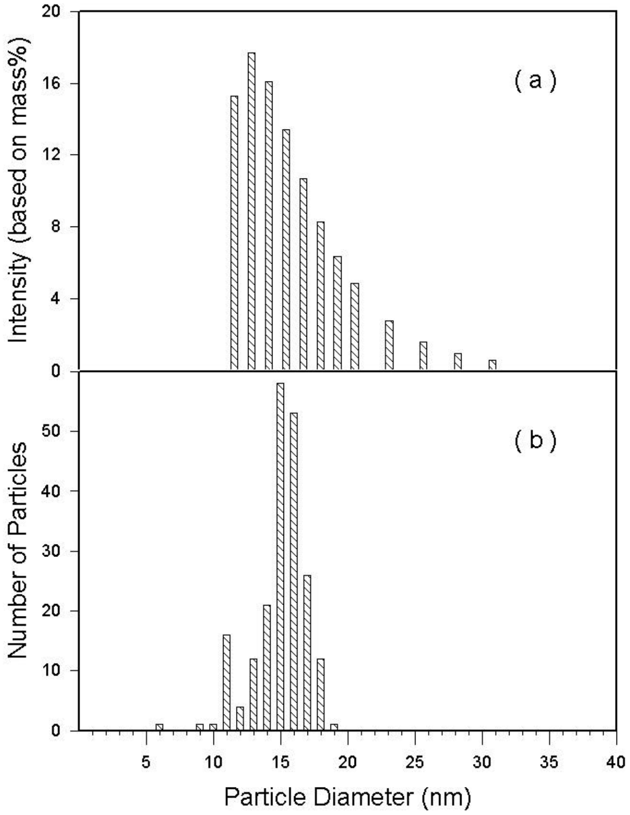


Figure 3. Bismuth particle size and size distribution measured from (a) dynamic light scattering and (b) TEM image.

essential to control this “force-balance” by finely tuning the ratio of TOP to oleic acid as well as the total amount of this combination. We have found that the molar ratio of TOP to oleic acid of 4:1 was optimal for our process. Oleic acid is indispensable as a stabilizing agent in this high temperature colloidal system; but too much oleic acid results in formation of bismuth agglomerates, possibly due to the polarity of oleic acid. Too high of a percentage of TOP also results in a failure of this preparation. We also investigated the effects of reaction temperature from 90 to 220°C, and we found that the optimum temperature should be 170 – 180°C when the other conditions were kept the same as stated above.

The particles prepared through above process can then be precipitated onto thin film by evaporation of the solvent and those associated ligands may be removed by heating in a vacuum oven [8,10]. Further work, which concentrates on the removal of the organic ligands to form an electrically continuous film of bismuth nanoparticles and subsequent measurement of electrical transport studies, is currently underway.

CONCLUSIONS

Highly crystalline and single domain bismuth nanoparticles have been successfully synthesized using a method concerning high-temperature reduction in organic solution. Size-selective precipitation of the original mixture results in colloids with a quasi-monodistribution of bismuth nanoparticles. Self-assembly of such nanoparticles into 2D pattern with short-range hexagonal order was, at the first time, obtained by capping the bismuth particles with phosphine ligand in a stable colloidal system containing non-polar solvent. During a reasonable period, these particles are still determinable as single-domain rhombohedral crystallites without oxidation.

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