

Self-assembled bismuth nanocrystallites†

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Using a high-temperature organic solution reduction method, highly crystalline and single domain bismuth nanoparticles have been synthesized and self-assembled.

The semimetal bismuth is particularly interesting as a potential thermoelectric material because of its low effective mass, highly anisotropic Fermi surface and its potential to induce a semimetal–semiconductor transition with decreasing crystallite size.¹ Most previous work on low-dimensional bismuth has understandably focused on one-dimensional wires synthesized in rigid inorganic or polymer templates.^{2,3} 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.⁴ Recently, Foos *et al.*⁵ published an achievement in synthesizing 10 nm bismuth nanocrystallites protected against oxidation by the surfactant, again using reverse micelles. However, both of the above efforts were still far from the electrical measurement stage due to the gap between particles isolated by either polymer or surfactant; both of which are difficult to remove considering that the melting point of bulk bismuth is only 271 °C. It is, therefore, necessary to improve the methodology in processing bismuth particles. In this communication, we report, for the first time, our results on self-assembly of bismuth semimetal nanoparticles formed by reducing an organometallic bismuth salt with a protecting ligand at high temperature. The synthesis of bismuth nanocrystallites was carried out in dioctyl ether ($[\text{CH}_3(\text{CH}_2)_7]_2\text{O}$, a non-polar solvent with high boiling point), using standard organometallic reaction procedures with airless/moisture-less devices and commercially available reagents.‡

Fig. 1(a) and (d) show transmission electron micrograph (TEM) images of the bismuth particles. The particles have a spherical morphology with an average diameter of 15 nm with a statistical deviation of ± 2 nm. The particles assemble into a two-dimensional monolayer with local hexagonal order. The minimum spacing between particles is approximately 3 nm and uniform. The high resolution TEM image in Fig. 1(c) shows fringes from the continuous lattice structure of a typical crystallite. A selected area electron diffraction pattern is shown in Fig. 1(b), indicating that the bismuth particles possess high crystallinity and a single rhombohedral phase. The lattice plane distances calculated from the diffraction rings are consistent with those of rhombohedral (bulk) bismuth.

The presence of a single rhombohedral phase can be confirmed by investigating the X-ray diffraction (XRD) patterns, which are shown in Fig. 2(a)–(c). From the as-synthesized particles [coarse particles without size selection, Fig. 2(a)] to those after a 6th size-selection [Fig. 2(c)], all the bismuth samples exhibit a rhombohedral phase. No trace of an oxide phase was observed. We have estimated the particle size for each sample from the XRD line broadening of the (012), (104) and (110) peaks using the Scherrer equation.⁶ For the coarse particles, the average crystalline size is 33 nm. After the

first size selection, the resulting colloid contains 23 nm (average diameter) particles. The 6th size-selected fraction contains 15 nm particles. We also estimated the average particle size and size distribution by using a light scattering technique and from the TEM images by directly measuring the diameters of several hundred particles (ESI†). The size distribution of the 6th size-selected fraction of bismuth particles has also been determined using both dynamic light scattering and TEM techniques. It was found that the average particle diameter is 15 ± 2 nm. The TEM images also reveal that self-assembly only occurs when the colloid contains quasi-monodisperse particles. Comparison of the particle size determined from TEM to that determined from XRD suggests that our particles are single-domain crystallites. It is worth mentioning that rhombohedral bismuth is the only detectable phase in both our TEM observation and XRD data.

The formation of nanoparticles from a redox reaction in a 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. TOP (trioctylphosphine) was used as a capping agent in our synthesis to limit the growth of the particles. Oleic acid was also used as a stabilizing agent. It is generally accepted that TOP reversibly coordinates neutral metal surface sites, slowing but not stopping growth of particles; while oleic acid can assist TOP in stabilizing the system.^{7,8} The capping ligand allows the particles to be dissolved and manipulated in nonpolar solvents and prevents agglomeration and oxidation of the particles. The particles can then be precipitated by evaporation of the solvent and the ligand removed by heating in a vacuum oven.^{7,8} Of the number of possible interactions among bismuth particles in the colloidal system, the most important are the

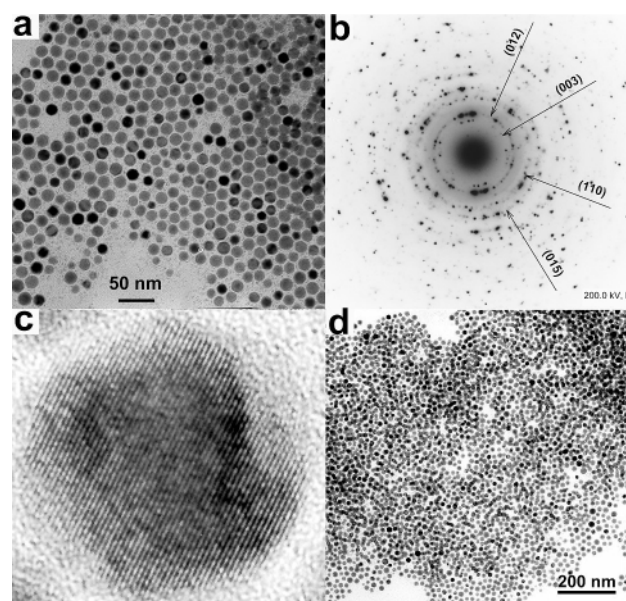


Fig. 1 TEM images of Bi nanoparticles: (a) collection of particles showing short-range hexagonal order, (b) selected area electron diffraction pattern, (c) high resolution image of a 15 nm particle and (d) low resolution view of one- and two-layer assembled particles.

† Electronic supplementary information (ESI) available: Fig. S1: size histogram of bismuth nanocrystallites. See <http://www.rsc.org/suppdata/cc/b1/b106105b/>

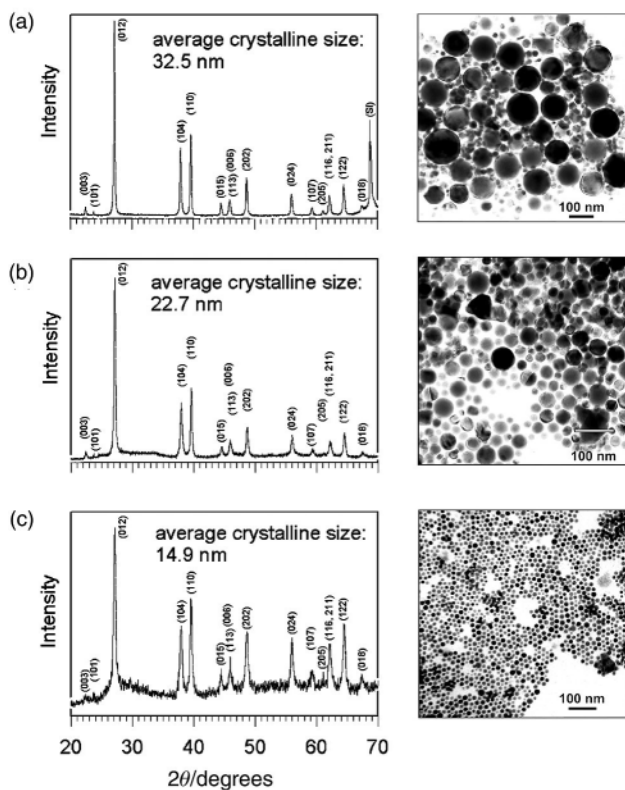


Fig. 2 XRD and TEM of Bi nanoparticles: (a) as-synthesized, (b) after the 1st size-selection and (c) after the 6th size-selection.

attractive van der Waals forces and the much shorter range steric repulsion provided by the tails of the organic ligand. This allows the nanoparticles to condense into either hexagonal-close packed mesoscopic crystals or an amorphous structure. To obtain a close-packed assembly of nanoparticles and avoid aggregates, it is 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 a 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 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 was 170–180 °C when the other conditions were kept the same as stated above. To examine the effect on self-assembly from the capping ligands, bismuth nanocrystallites in hexane solution were investigated using a fluorescence photometer. With $\lambda_{\text{ex}} = 280$ nm as the excitation wavelength, both oleic acid and TOP give a fluorescence effect with different emission wavelengths (~ 364 and ~ 292 nm, respectively). The region of emission wavelength of capped-bismuth sample that is able to be self-assembled is close to that of TOP (~ 284 nm). As stated in the experimental footnote, the particle size distribution was refined by repeated cycles of titrating the colloid with ethanol, precipitating the particles by centrifugation and redispersing in hexane. Self-assembled patterns of nanocrystallites were obtained only for those samples that indicated the presence of TOP in the fluorescence spectra. After further 'washing' with ethanol and redispersing in hexane, the fluorescence from the sample showed no detectable trace of TOP and we were unable to obtain any ordered assembly pattern of nanocrystallites. This suggests that the TOP acts as a capping

agent and is essential for the formation of a self-assembled system.

In conclusion, highly crystalline and single domain bismuth nanoparticles have been successfully synthesized using a method of high-temperature reduction in organic solution. Size-selective precipitation of the original mixture results in colloids with a quasi-monodistribution of bismuth nanoparticles. Further, we have demonstrated, for the first time, self-assembly of semimetal nanocrystallites into a 2-D pattern with short-range hexagonal order. These nanocrystallites are capped with a phosphine ligand (TOP) and are stable in a colloidal system containing a nonpolar solvent. Upon evaporation of the solvent, the particles are still present with TOP and are stable in air for a short time. Further work, which concentrates on the removal of the organic ligand to form an electrically continuous film of bismuth nanoparticles and subsequent measurement of electrical transport studies, is currently underway.

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Notes and references

‡ *Experimental*: in the synthetic approach, dioctyl ether was selected as the high boiling point reaction medium. Bismuth 2-ethylhexanoate, soluble in dioctyl ether, was used as the bismuth precursor. LiBEt_3H (super-hydride) was used as the reducing agent. However, commercial LiBEt_3H is supplied in a tetrahydrofuran (THF) solution. Since THF is a polar solvent, it must be completely removed and replaced by dioctyl ether under inert gas before use.^{7,8} A typical experiment involved a total of about 25 ml of solution. A freshly-prepared solution of bismuth 2-ethylhexanoate in dioctyl ether (0.2 M, 2 ml) and oleic acid (in a molar ratio of 1 : 10) was added to a three-neck flask, which contained 20 ml of dioctyl ether, under flowing argon. The temperature was raised to 100 °C and TOP (molar ratio of TOP to oleic acid fixed at 4:1) was injected into the solution with a syringe while stirring in argon. The temperature was further increased up to the reaction temperature (normally 175 °C). Reduction of bismuth took place by injecting 0.5 M LiBEt_3H in dioctyl ether (3 ml). 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 then quickly taken into the glovebox and the mixture was subsequently cooled to room temperature. Particles were precipitated by adding ethanol (40 ml) to the system and collected by centrifugation under argon atmosphere. The precipitate was then re-dispersed into hexane (15 ml). Particle size selection of the original colloid was performed by titration of ethanol as a polar solvent into the hexane colloid, following the standard technique.⁷ Adding the ethanol caused the largest particles to flocculate, and this mixture was separated by centrifugation. This fractionation was repeated to produce several size distributions.

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